Computational Study of DNA-Directed Self-Assembly of Colloids

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Computational Study of DNA-Directed Self-Assembly of Colloids

Abstract
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In the first part of this thesis, we studied the interfacial dynamics during colloidal crystallization. The interfacial dynamics of binary crystals was probed by weak impurity segregated growth. This segregated growth was interpreted as the number of surface bonds required to crystallize a fluid particle. For short-ranged DNA-mediated interactions, an integer number of surface bonds are needed for a particle to crystallize, which was verified by experiments. This demonstrates the utility of our computational framework to replicate growth kinetics of DNA-directed particle self-assembly.

In the second part of this thesis, we studied the kinetic control of crystal structure in DNA-directed self-assembly. For a dilute colloidal suspension, with weak intermolecular interaction between similar particles, binary crystals can assemble into close-packed (cp) or body-centered-cubic (bcc) structures based on thermodynamic or kinetic factors. Under fast kinetic conditions bcc crystals assemble from the suspension. For the same intermolecular interactions and slow kinetic conditions, cp crystals are observed within the suspension.

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COMPUTATIONAL STUDY OF DNA-DIRECTED SELF-ASSEMBLY OF COLLOIDS

Raynaldo Theodore Scarlett

A DISSERTATION

in

CHEMICAL AND BIOMOLECULAR ENGINEERING

Presented to the Faculties of the University of Pennsylvania in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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Computational Study of DNA-Directed Self-Assembly of Colloids

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ABSTRACT

COMPUTATIONAL STUDY OF DNA-DIRECTED SELF-ASSEMBLY OF COLLOIDS

Raynaldo Theodore Scarlett

Dr. Talid Sinno

Immense insight into fundamental processes necessity for the fabrication of nanostructures is gathered from studying the self-assembly of colloidal suspensions. These fundamental processes include crystal nucleation and particle aggregation. In this thesis, we developed an efficient computational framework to study the self-assembly of same-sized, spherical colloids with intermolecular interactions, such as the programmable DNA-mediated interaction.

In the first part of this thesis, we studied the interfacial dynamics during colloidal crystallization. The interfacial dynamics of binary crystals was probed by weak impurity segregated growth. This segregated growth was interpreted as the number of surface bonds required to crystallize a fluid particle. For short-ranged DNA-mediated interactions, an integer number of surface bonds are needed for a particle to crystallize, which was verified by experiments. This demonstrates the utility of our computational framework to replicate growth kinetics of DNA-directed particle self-assembly.
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Chapter 1

Introduction

Colloidal self-assembly is the autonomous organization of particles to form aggregates or ordered structures. For decades, colloidal self-assembly have been used to study phase transitions from crystallization [34], gelation [66], nucleation [6, 84], and sublimation [92]. These processes are ubiquitous in nature and are directly observable for micro-sized colloids [34, 92]. Another attractive feature of colloidal self-assembly is that suspensions of colloids can be simultaneously studied by three different approaches: experiments, simulations, and theory. Here, useful insights gathered from simulations and theory can be verified by experiments. Experiments can serve as input to simulations and theory. The flow of information between methods makes colloidal self-assembly an ideal approach for building novel nanostructures and devices [50], as potential fabrication bottlenecks can be identified by simulations [59, 67]. The aim of this work is to develop a computational framework that can identify accessible nanostructures for a given colloidal suspension, in particular colloids that self-assembly via DNA-mediated interactions.
1.1 Design of Colloidal Self-Assembly

There exist an infinite amount of possible colloidal assemblies which can self-organize resulting in an immense design parameter space. The parameter space for designing colloidal self-assemblies, as shown in Fig. 1.1, is defined primarily by the type of colloidal interaction and the geometry of the colloids within the assembly. Colloids can experience intermolecular interactions (arising from the presence of an adjacent colloid) or external interactions (caused by an external source other than an adjacent colloid).
Colloids within the assembly can be selected to have a single type, engineered to have a desired geometry, or have multiple types with differing geometries.

### 1.1.1 Engineered Colloidal Building Blocks

The simplest geometry for a colloid is the hard-sphere (HS), where the distance from the center to the surface of the particle is the same in all directions (isotropic). HS have no intermolecular interactions, and single component HS without external interactions are located at the origin of our design parameter space (Fig. 1.1). The phase behavior of same-sized HS is studied extensively in the literature, first by theory [43] and then verified by experiments [84]. The phase behavior depends only on the volume or packing fraction, \( \phi \equiv \rho \pi \sigma^3 / 6 \), where \( \rho \) is the number density of the spheres and \( \sigma \) is the diameter of the spheres. Same-sized HS undergo a fluid-solid transition at \( \phi = 0.494 \) and melting transition at \( \phi = 0.545 \), due purely to entropy [31]. The entropy of the system is given by the volume available per particle. There are three crystal lattices that may assemble from the HS fluid: (1) face-centered cubic (fcc) lattice, (2) hexagonal close packed (hcp) lattice, and (3) random hexagonal close packed (rhcP) lattice. The HS phase diagram is useful as a reference for understanding the phase behavior of systems with short-ranged interactions.

As fabrication techniques for colloidal particles become more refine, the geometry of particles become more exotic (increase in the degree of anisotropy) as compared to HS. A representative amount of these anisotropic particles are shown in Fig.
1.2. Now, colloids can be synthesized to form branched [69], faceted polyhedra [68] and patterned particles [47]. These colloidal particles can be parameterized within an ‘anisotropic space’, comprised of different degrees of roughness, shape gradient, patterning, and branching [35]. Theory, simulations, and experiments can study the self-assembly of anisotropic particle based on their location within the anisotropic space. Challenges toward self-assembly of these particles include steric and packing restrictions on their organization [21, 37, 102]. Currently, phase diagrams for a vast amount of the anisotropic space are unknown as theory and experiments face these challenges. Simulations may provide key insights and guidance for theory and experiments. The reward for assembling anisotropic particles is great, as they form a more diverse set of potential nanostructures.

Figure 1.2: Representative examples of recently synthesized anisotropic colloids. Figure is taken from ref. [35].
1.1.2 Colloidal Interactions

The introduction of colloidal interactions, whether intermolecular or external, into the suspension provides another approach to increase the diversity of assembled structures. The simplest system with a colloidal interaction is comprised of same-sized HS particles. These particles in equilibrium corresponds to a one-component classical system with an isotropic pair potential, \( E(r) \), in the absence of any external field. The total intermolecular interaction is given as

\[
U(x^N) = \frac{1}{2} \sum_{i \neq j}^{N} E \left( |x^i - x^j| \right), \quad (1.1)
\]

where \( x^i \), \( i = 1, \ldots, N \) is the three-dimensional position vectors of \( N \) particles and the distance between particles is given by \( r = |x^i - x^j| \). Typical examples of \( E(r) \) are HS for sterically stabilized suspensions and electrostatic for charge-stabilized suspensions [46].

Now, the same system can be studied with external interactions coupled to the center of the particles. The external energy is given as

\[
U_{\text{ext}}(x^N) = \sum_{i=1}^{N} E_{\text{ext}} \left( x^i \right). \quad (1.2)
\]

To ensure that the colloidal particles within the system only experience the applied external interaction, as described by expression (1.2), the solvent and particles must have the same density allowing for no particle sedimentation within system. The applied external interaction can be categorized into two groups: (1) acting through a static solvent
(no deformation of the solvent) and (2) acting through a dynamic solvent. For the first group, particles align themselves in the direction of the applied interaction and some of these interactions are induced by laser-optics, magnetic, and electric fields. For the second group, particles aggregate by deformation of the solvent, such as shear and solvent evaporation. An in-depth review of these external interactions is presented in refs. [29, 65, 114].

In this work, the computational framework for studying colloidal self-assembly is developed for same-sized HS suspensions with intermolecular interactions defined by expression (1.1). This step is taken to simplify the development of the framework. However, more complex, engineered, colloidal building blocks and external interactions can be easily added to the framework at a later date.

1.2 Classic Intermolecular Colloidal Interactions

1.2.1 Depletion Interaction

In a colloidal suspension containing particles of two very different sizes, an attractive force between the larger particles is generated. This force, which is purely entropic in nature, arises because of the extra volume that becomes available to the smaller particles when two large particles approach each other. As shown in Fig. 1.3, each of the larger particles (diameter σ) is surrounded by a spherical shell that is inaccessible to the smaller
particles (diameter $\delta$). For a fixed number of particles, the total excluded volume in the system is decreased by overlaps created as the larger particles approach each other. A schematic of this effect, which is known as depletion [5], is shown in Fig. 1.3.

The phase diagram associated with a depletion-driven system is more complex than the hard-sphere system. Here, the phase diagram contains gas, liquid, and solid phases due to the presence of attractive forces between the larger particles [31].

The range and strength of the interaction force between two particles depends on the size ratio ($\alpha = \delta/\sigma$) of the two particle types and on the concentration of the depletant (small particles) [24, 31, 85]. As $\alpha$ increases, the range of attraction increases, while an increase in depletant concentration increases the strength of the attraction. Direct simulation of a depletion system is computationally intractable due to the large timescale differences associated with particles of very different sizes [26]. A common approach to address this difficulty is to coarse-grain out the small particles and derive an effective interaction potential between the large particles as first proposed by Asakura-Oosawa [5] and later modified by Vrij [107].
1.2.2 Electrostatic Interaction

Electrostatic interactions can be short or long-ranged, relative to the diameter of the colloid, and varies from weak to very strong (several hundred $k_B T$). The interaction between oppositely charged particles, counter-ions, is attractive, while a repulsive interaction occurs between particles with the same charge, co-ions. The electrostatic interaction is affected by the solvent relative permittivity, as the solvent can influence the flow of electrons between particles through its ionic concentration.

The simplest short-range electrostatic interaction is the non-specific, van der Waals interactions. Here, the interaction ranged from 0 to 10 nm [46] and arises due to the ever present electron fluctuations within each particle [46, 94]. This attractive interaction is the primary cause for uncontrolled aggregation in colloidal suspension and
is commonly minimized by steric stabilization (or repulsion, a short chain-like molecule is attached to the colloid’s surface).

Colloidal suspensions of counter-ions interact through screened Coulomb (Yukawa) interaction. The Yukawa pair potential is \( E(r) \approx \lambda \exp(-\kappa r)/r \), where \( \lambda \) is the potential strength and \( 1/\kappa \) is the Debye-Huckel screening length. This system exhibits a fluid phase as well as a solid phase comprising of face-centered cubic (fcc) and body-centered cubic (bcc) as a function of \( \lambda/k_B T \).

1.3 DNA-Mediated Interaction

Suspensions of spherical colloids with depletion and electrostatic interactions self-assemble into limited nanocrystals, such as fcc, hcp, rhcp (obtained from the HS system), and bcc. The morphological diversity of assembled crystals from these suspensions is greatly improved with the introduction DNA-mediated interactions [1, 95]. DNA is the premier material for designing novel structures through its nanoprecision and tunability.

1.3.1 Specificity and Tunability of DNA-Assembly

The specificity and tunability of DNA-assembly arise from the assignment of the DNA base pair sequence. The DNA sequence is comprised of four different base: adenine (A), cytosine (C), guanine (G), and thymine (T). DNA hybridization energy exists between
two DNA sequences as a result of complementary binding of base pairs AT and GC, or mismatched binding. Complementary binding of two single DNA sequences (strands) forms double helices.

Amazing curvatures and structures can be assembled with nanometer precision through careful design of the DNA sequence and length. DNA curvatures can be controlled in a synthetic system by self-assembly of axis-aligned and laterally coupled long and short double helices [25], as schematically shown in Fig. 1.4 a. One approach to assembly DNA structures is based on the “scaffolded DNA origami” technique [90]. This technique requires that a long single-stranded of DNA is laid out in a 2-dimensional (2D) plane following a designated folding path. Then hundreds of short “staple strands” hybridize with the scaffold strand through complementary base pairing to form branched DNA junctions between adjacent helices. As shown in Fig. 1.4, this technique can form 2D structures such as stars and smiley faces (Fig. 1.4 b) or 3D nanoshapes (Fig. 1.4 c). Also, 3D polyhedral objects can be assembled from DNA branched junctions, Fig. 1.4 d.
Figure 1.4: DNA-assembled structures. In 2-dimension (2D), DNA-assembly controls curvature (a) [25] and DNA-origami (b) [90]. In 3D, DNA also controls the assembly of engineered nanoshapes (c) [28] and polyhedrons (d) [40].

1.3.2 Directed Self-Assembly of DNA-Functionalized Colloids

The programmability of DNA can be harnessed for the assembly of spherical colloids by the design of DNA-functionalized colloids. Here, the surface of the colloid is modified by the addition of single strands of DNA. The interaction between these colloids is driven by the DNA hybridization energy within each bridge (i.e. binding between two DNA strands on opposite colloids) and the average number of bridges formed.

Theoretical predictions show that DNA-functionalized colloids assemble into a diverse set of crystalline structures [101]. In 2005, Crocker and co-workers [11] carried out the first experiments of DNA-functionalized colloids that self-assembled into ordered
(rhc0) crystals. They noted that weak, reversible interactions are needed to form ordered crystals, allowing for annealing of the assembled colloids via thermal fluctuations. As shown in Fig. 1.5, there exist two constructs for designing the DNA-hybridization energy between colloids: assisted or direct bridge formation between strands of DNA on opposite particles. For the assisted bridge formation construct, binding between strands of DNA on the colloid surface (spacers) is assisted by a linker sequence of DNA within the suspension. For the direct bridge formation, spacers on interacting colloids directly bind with each other. Both approaches are capable of tuning the DNA-interaction strength and defining multi-component systems. However, the assisted bridge formation allows for faster and multiple design iterations of directed self-assembly by engineering the linker sequence.

**Figure 1.5:** Constructs for designing DNA-mediated interactions.
The versatility of DNA-modified colloids to investigate fundamental processes important to nanofabrication is outlined in Fig. 1.6. These functionalized particles can be directed to form ordered 2D and 3D structures across both the nanometer and micrometer lengthscales. In 1996, the first realization of these systems resulted in the formation of aggregates [74], Fig. 1.6 a. Nearly a decade after this initial work, the first ordered crystals are obtained [11], Fig 1.6 d. In ref. [11], the authors demonstrated that weak, reversible interactions near equilibrium are required to self-assemble ordered crystals. Building on the preceding work, in 2008, DNA-directed self-assembly of gold nanoparticles formed BCC superlattices [79, 81], Fig. 1.6 b. The authors designed two sub-populations of particles where opposite and similar particles attract and repel each other, respectively. This work is significant because it is the first experimental evidence of DNA-modified colloidal crystals that can not be assembled from the simple HS interaction.

Instead of bulk self-assembly, another approach for obtaining novel nanostructures is directed-assembly on ordered templates [16, 63]. Here, fluid particles can preferentially bind to specific region along the template. Crystals could potentially grow from ordered template and retain the order of the template. One method for designing 2D arrays of ordered DNA-functionalized colloids is outlined in ref. [16], Fig. 1.6 c.

As the push to fabricate exotic nanocrystal accelerates, the potential kinetic barriers toward ordered assembly of these systems remains and is currently poorly understood. Recently, Kim and co-workers demonstrated how interfacial kinetics affect
the growth of ordered crystals [59], Fig. 1.6 e. We showed through detailed Monte Carlo simulations and experiments that a fixed number of DNA-bridges within the interface are required to permanently attach a fluid particle to a growing crystal.

**Figure 1.6:** The investigation of fundamental processes for nanofabrication through DNA-functionalized colloids. The DNA-directed colloids form aggregates (a) [74], crystals (d) [11], superlattice crystals (b) [79, 81], and solid solution crystals (e) [59]. DNA-functionalized colloids are designed to form 2D ordered arrays (c).

### 1.4 Crystal Nucleation and Growth

Self-organization into novel crystalline structures is dependent on crystal nucleation and growth. Here, the morphology of a critical cluster (or crystal) determines the morphology of the assembled crystal. The critical cluster is the cluster at which the energetic gains for expanding the cluster is equal to the energetic cost for forming an
interface between the cluster and fluid. If the size of the critical cluster is small (~ few particles) then multiple critical clusters may form in the suspension leading to the assembly of disordered structures such as aggregates.

1.4.1 Classical Nucleation Theory

Nucleation is a ubiquitous phenomenon present in everyday life, from the freezing of water into ice crystals to the condensation of water droplets upon a cold glass of beer. A semi-quantitative understanding of crystal nucleation is given by classical nucleation theory (CNT). CNT assumes that the properties of the new phase can be modeled as a macroscopic phase. According to CNT, the process of forming a nucleus requires work to form an interface between the new and parent phases. This energetic requirement is offset by the reduction of the (volume) free energy upon formation of the new phase. For the former, the free energy cost is proportional to surface area of the nucleus, while the latter is proportional to the volume of the nucleus. For a given volume, the nucleus surface area is minimized by a spherical nucleus. Therefore, the free energy change due to nucleation can be modeled by

$$\Delta G = \frac{4}{3} \pi r_{\text{nuc}}^3 \rho_s \Delta \mu + 4 \pi r_{\text{nuc}}^2 \gamma_{\text{nuc}},$$

(1.3)

where $r_{\text{nuc}}$ is the radius of the nucleus, $\rho_s$ is the number density of the nucleus phase, $\Delta \mu$ the difference in chemical potential between the parent and nucleus phases, and $\gamma_{\text{nuc}}$ is the interfacial free energy density between the two phases. A schematic of the free
energy as a function of nucleus size is given by Fig. 1.7, where the solid lines are defined by eq. (1.3).

The cluster size at which there is a balance between the surface and volume free energy contributions is called the critical cluster size, where the free energy is given by

$$\Delta G_{\text{crit}} = \frac{16\pi}{3} \frac{\gamma_{\text{nuc}}^3}{\left(\rho_s |\Delta \mu|\right)^2}. \quad (1.4)$$

Clusters smaller than the critical radius tend to shrink as the interfacial free energy required to keep the cluster intact is larger than the gain in volumetric free energy. While clusters larger than the critical radius tend to grow as addition of particles to the cluster decreases the free energy of the cluster (i.e. gains from volumetric free energy is larger than losses due to interfacial free energy).

**Figure 1.7:** A schematic of the free energy described by classical nucleation theory. The green line is a sketch of eq. (1.3). For a move from the solid to dotted green curves, the size of the critical radius increases as the surface free energy contribution dominates expression (1.3). While an increase in the volume free energy decreases the size of the critical radius, a move from the solid to the dashed-dot curves.
1.4.2 Crystal Growth

Crystal growth leads to the development of stable crystals by the attachment of growth particles to a post-critical cluster. These growth particles traverse the fluid-crystal interface to attach to a growth site on the crystal surface. The growth sites on the crystal surface are comprised of flats, steps, and kinks sites [91]. As shown in Fig. 1.8, for a simple-cubic lattice, growth particles attach to a growth site via one, two, or three nearest neighbor bond(s) for the flat (f), step (s), and kink (k) site, respectively. With particles attaching to growth sites, the crystal can grow normal to its surface by a rate of displacement, \( \tau \), and also along its surface by a rate of displacement, \( \varsigma \). If the binding energy per pair of particles is \( E_b \), then the corresponding binding energy for a growth particle to the flat, step, and kink sites is \( E_b \), \( 2E_b \), and \( 3E_b \), respectively. The probability of capturing a growth particle at any site is given as

\[
\exp\left(-\frac{nE_b}{k_B T}\right), \tag{1.5}
\]

where \( n \) is the number of bonds between the particle and site. From expression (1.5), the probability of binding to a kink is higher than binding to a step, due to its higher binding energy. As a result, the crystal rates, \( \tau \) and \( \varsigma \), are strongly dependent on the contribution of binding to a kink site.
From the above considerations, the kinetics of crystal growth may, in general, be considered to occur in the following stages:

1. Transport of growth particles to the crystal surface by bulk diffusion and their capture on the crystal surface (i.e. attachment to a flat site).
2. Migration of growth particles from a flat site to a step site (and vice versa).
3. Migration of growth particles from a step site to a kink site (and vice versa).

One or more of the above stages may control the crystal growth rate, but the slowest one is called the rate-limiting step. The growth kinetics as characterized by $\tau$ and $\varsigma$ depends on the crystal structure, the structure of the fluid-crystal interface, the presence of defects, and impurities on the crystal surface. The difference in $\tau$ for different surfaces determines the overall shape of the crystal. Under slow growth kinetics, different segments of the crystal surface will have commensurate values of $\tau$ resulting in uniform growth of the crystal. The growing crystal maintains a spherical shape. Under fast growth kinetics, a distribution of $\tau$ is established on the crystal surface resulting in
uneven growth such as branches, lobes, or step defects. These crystalline shapes are typically formed during dendritic growth.

1.5 Thesis Objective and Outline

The purpose of this thesis is to develop an efficient computational framework capable of determining whether a given colloidal suspension can self-assemble into a desired nanostructure. Currently, the scope of the framework is limited to same-sized spherical colloidal suspensions with no external interactions. The computational framework has two main components: (1) simulating dynamical processes within a colloidal suspension such as particle aggregation, and (2) determining the thermodynamics of assembled crystals.

The contents of this thesis are discussed in four chapters. In chapter 2, we apply detailed simulations to determine the impact of interfacial growth kinetics on the crystal assembly. This is accomplished by tracking the crystallization of tracer fluid particles. As the probability of binding a tracer particle to the crystal surface, expression (1.5), is equal to the segregation coefficient of the tracer particle. The segregation coefficient is the ratio of the tracer particle concentration in the bulk crystal to fluid. In chapter 3, we investigate both the kinetics and thermodynamics of superlattice assemblies comprised of DNA-modified colloids. Here, the colloidal suspension consists of two sub-populations of same-sized particles. Recent, experiments of this system demonstrated, for the first time, that bcc superlattices can self-assemble out of suspension. However, the
mechanism for self-assembly of this superlattice is still up for debate. We apply our computational framework to elucidate the assembly mechanism of these systems. Finally in chapter 4, we summarize key findings of this work and purpose possible extensions to the computational framework.
Chapter 2

Computational Analysis of Interfacial Dynamics during Colloidal Crystallization with DNA-Mediated Interactions

2.1 Introduction

Colloidal models have provided considerable insight into a variety of fundamental processes related to particle aggregation, including crystal nucleation [7, 34], morphology [18], melting [4, 92], and growth [18, 34]. By virtue of their size (nanometer to microns) and well-defined interactions, colloidal models can provide useful platforms for probing subtle mechanistic elements related to aggregation in atomic systems. In addition to serving as a model system, colloidal assembly technology is now sufficiently versatile and controllable to provide a host of promising approaches for fabricating novel materials with useful properties (e.g. optical metamaterials).
The assembly of colloidal crystals using engineered interparticle interactions has now been demonstrated experimentally in a variety of particle types and sizes. There are numerous approaches for engineering interactions between colloidal particles including direct particle modification [11, 78] and induction by external fields [65]. Examples of interparticle interaction sources that have been successfully realized in experiments include depletion [58], and electrostatic [62] and magnetic [115] fields. One extremely promising route for colloidal assembly relies on the use of grafted brushes comprised of single-stranded DNA oligomers, as shown schematically in Fig. 3.1. In this approach, the single-stranded DNA sequences are engineered to either be partially self-complementary [11, 58, 59, 78], or to be partially complementary to another “linker” oligomer that is introduced into the solution containing the engineered particles. Both approaches have been shown to drive colloidal crystallization under the appropriate conditions of total particle volume fraction, system temperature relative to the DNA melting point, and particle size relative to the DNA oligomer length. A key advantage of DNA-mediated interactions is their specificity, which in principle enables a systematic approach for fabricating multicomponent assemblies with an arbitrary number of different particle “types”.

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Figure 2.1: Schematic representation of two variants of DNA-mediated colloidal assembly systems in which particles are modified by grafting DNA oligomers onto their surfaces. (a) Direct bridge system, (b) linker-mediated system. S = spacer oligomer, L = linker oligomer.

Much theoretical emphasis has been placed on the prediction of equilibrium phase diagrams for assembly as a function of interparticle interaction characteristics, while relatively little consideration has been directed towards growth kinetics and the related problem of defect formation. A host of literature studies have sought to increase the range of accessible assembly structures by manipulating particle shape [70], pre-assembling building blocks with desired symmetries [35], and theoretically predicting interaction models [101] that would lead to interesting assemblies. Nonetheless, it is well understood that the incorporation of particles into a growing crystal is controlled by both
thermodynamic and kinetic factors at the crystal interface [10, 48]. For example, recent theoretical [64, 67] and experimental [59, 78] studies highlight the importance of the growth kinetics for realizing high-quality DNA-colloidal assemblies that are consistent with the predicted equilibrium phase.

In this paper, we study computationally the growth of binary solid-solution (close-packed) colloidal crystals in which particle assembly is driven by DNA-mediated interactions. In particular, we analyze the effect of growth kinetics on the binary segregation process at the crystallization interface using a model that is closely connected to an actual experimental system [11, 58, 73]. Using detailed Monte Carlo (MC) and Brownian dynamics (BD) simulations, we construct simple mechanistic models to describe the process of interfacial segregation that appears to be generically applicable to a broad variety of material systems. The remainder of the paper is outlined as follows. In Section 2.2, we provide brief details of the experimental system upon which the present study is based and the associated pair potential model used in the simulations. In Section 2.3, we describe the various simulation methods employed. Results and associated discussion are presented in Section 2.4. In Section 2.5, the MC results are further interpreted in the context of BD simulations, and finally, conclusions are presented in Section 2.6.
2.2 Experimental System for Binary Solid-Solution

Crystallization

The experimental system on which the present computational study is based consists of an aqueous suspension of two mixed populations of micron-sized (diameter, $\sigma = 0.98 \mu m$) polystyrene spheres, ‘A’ and ‘B’, that are essentially identical in their preparation and physical parameters, but which bear short grafted strands of single-stranded DNA strands whose sequences differ by a single nucleotide [59]. Further experimental details regarding the DNA grafting procedure and particle fabrication are given in refs. [57, 58]. In the following sections, interactions between two $A$ particles always are assumed to be stronger than those between one $A$ and one $B$ and between two $B$ particles, i.e. $E_{AA} > E_{AB} > E_{BB}$, where $E_{XY}$ is the maximum value of the DNA-induced sphere-sphere binding energy.

In the absence of DNA hybridization, the 65-base grafted DNA strands create a soft repulsion between the microspheres’ surfaces, with an approximately 10 nm range. When additional ‘linker’ DNA strands containing two complementary sequences are added to the solution, hybridization leads to the formation of DNA bridges between particles, pulling them together as shown in Fig. 2.1. At temperatures where this hybridization is reversible, bridges form and dissociate continuously. This allows particles to bind and unbind dynamically from one another, producing a time-averaged attractive interaction having a $\sim 15$ nm range. The strength of the interaction is modulated
by both the temperature and the specific sequence of the oligonucleotides used to define the spacer and linker molecules. A summary of the main features of a quantitative model for the induced pair potential between two microspheres is provided next in order to introduce concepts that will be required to further define the system we study here.

### 2.2.1 Pair-Potential Model for DNA-Mediated Interactions

A pair-potential function for the binary system outlined in the previous section was developed previously by Biancaniello et al. [11]; a summary of the main features of the interaction potential model are provided here for reference. This interaction model has been verified by comparison to experimental measurements of the separation statistics between two microspheres held in a linear optical tweezer [11].

The DNA-functionalized colloids are modeled as spheres surrounded by a ‘cloud’ of spacers of thickness $L$, where $L$ is the contour length of the grafted DNA spacers (see Fig. 2.1). Near contact, molecule bridges ($sls$) are formed between particles as their spacer clouds overlap. The attraction between spheres, $E_a$, has a range of $h < 2L$, where $h$ is the surface-to-surface separation between spheres. $E_a$ results from the enthalpy of DNA hybridization within $sls$ bridges. Spacers only form the $sls$ bridge with a linker at their terminal end. With the assumption of low DNA density on the surface of the sphere, intra-DNA-DNA interactions along the spacer are negligible. Therefore, DNA on one sphere colliding with the opposing sphere produces a repulsion, $E_r$, of range $h < L$. The net pair-potential between colloids can be written as $E = E_a + E_r$. 

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The geometry of the particles encompassing the overlap region can be modeled as flat plates, as the radius of the equal sized spheres, $\sigma / 2$, is larger than $2L$. The derived net potential between flat plates can be converted to two sphere geometry using the Derjaguin approximation [46]. Let $P_h(x)$ be the probability distribution of the height of the grafted polymer, then the entropic repulsion per unit area, $A$, due to DNA compressed between the plates is [27]

$$\frac{E_r(z)}{A} \approx -2\sigma k_BT \ln \int_0^z P_h(x) dx,$$

(2.1)

with $\int_0^L P_h(x) dx = 1$, where $z$ is the surface-to-surface distance between flat plates instead of spheres, $x$ is the distance away from the plate and $\sigma_s$ is the surface density of the grafted DNA spacers. Since we are assuming that DNA-DNA interactions are negligible, $P_h(x)$ corresponds to the height distribution of a single grafted polymer.

The attractive contribution to the interaction is an equilibrium average of the number of $sls$ bridges. If each spacer has the same, statistically independent, probability, $p$, of forming a bridge at a given separation, then the probability that no bridges are formed is $P_{\text{free}} = (1 - p)^{N_s}$, where $N_s$ is the number of spacers on a plate within the overlap region. The probability that one or more $sls$ bridges are formed is $P_{\text{bound}} = 1 - P_{\text{free}}$. Now, the attractive interaction is defined by the free energy of forming a bridge, $E_a(z) = -k_BT \ln \Omega$, where $\Omega$ is the partition function for all possible bridged states relative to the free
state at a given \(z\). In other words, \(\Omega = \sum_{i=0}^{N_s} \frac{P_i}{P_{\text{free}}} = 1 + \frac{P_{\text{bound}}}{P_{\text{free}}}\), where \(P_i\) is the probability \(i\) bridges form between the plates for a given \(z\). To ensure that \(E_a(z>2L) = 0\) holds for non-interacting spheres (i.e. no overlap region), the zero bridge probability is included in \(\Omega\). Now, the attractive interaction becomes

\[
E_a(z) = -k_B T \ln \left(1 + \frac{P_{\text{bound}}}{P_{\text{free}}} \right) = k_B T N_s \ln(1-p) \approx -k_B T N_s p = -k_B T \langle N_{\text{sls}} \rangle, \quad (2.2)
\]

for \(p << 1\). The above interaction is simply the product of the thermal energy of the suspension \((k_B T)\) and the average number of \(\text{sls}\) bridges, \(\langle N_{\text{sls}} \rangle\), that are in chemical equilibrium at separation \(z\).

Within the overlap region, of volume \(\Delta V\), DNA-mediated bridges dynamically form and break according to the following chemical reaction: \(s + l + s \leftrightarrow \text{sls}\), where \(s\) is the spacer grafted onto the surface of the colloid and \(\text{sls}\) is the bridge DNA complex that mediates the interaction. The chemical equilibrium for this reaction is given as

\[
K_{eq} = \frac{c_{\text{sls}}}{c_s c_l c_s} = \exp\left(-\Delta G / k_B T\right), \quad (2.3)
\]

where \(c_i\) is the concentration of species \(i\), \(K_{eq}\) is the equilibrium rate constant and \(\Delta G\) is the change in Gibbs free energy due to the formation of a single \(\text{sls}\) bridge [12]. The average \(\text{sls}\) bridges within the overlap region is defined as \(\langle N_{\text{sls}} \rangle = c_{\text{sls}} \Delta V\); however, \(c_s\) is
not spatially distributed uniformly within $\Delta V$. To compensate for this inhomogeneity image dividing $\Delta V$ into sub-volume of $dv_i$, where $c_{s,i}$ in *each* sub-volume is assumed to be spatially distributed uniformly. Now, the average number of *s/s* bridges between plates is

$$\langle N_{ss} \rangle = \frac{\exp\left(\frac{-\Delta G}{k_BT}\right)}{c_0^2}c_i \sum_i c_{s,i} dv_i,$$

(2.4)

where $c_0 = 1$M is a reference concentration. If the overlap volume between plates is sectioned into infinitesimal sub-volume units and $c_s(x) \propto \sigma_s P_s(x)$, then the above expression for the average number of *s/s* bridges becomes

$$\langle N_{ss} \rangle \propto A c_i \sigma^2_s \frac{\exp\left(\frac{-\Delta G}{k_BT}\right)}{c_0^2} \int_0^z P_s(x)P_s(x-z) dx,$$

(2.5)

for $dv = A \, dx$. $P_s(x)$ is the probability distribution of finding the end of the spacer at $x$ relative to its anchored point. Also, $P_s(x)$ is normalized such that $P_s(x) dx = c_s(x) / \sigma_s$. For flexible spacers, $P_s(x)$ is determined numerically from a random walk simulation consisting of $L / K_L$ steps of length $K_L$, where $K_L$ is the Kuhn length of a single stranded DNA [12]. For rigid spacers, DNA double helices with functional terminal end attached to the colloid’s surface, $P_s(x)$ is equal to $1/L$ for $x < L$. Finally, the attraction interaction between two plates is given as
\[
\frac{E_a(z)}{A} \approx -c_i \sigma^2 k_B T \frac{\exp(-\Delta G / k_BT)}{c_0^2} I(z), \quad (2.6)
\]

\[
I(z) = \frac{\int_0^z P_s(x) P_s(x-z) \, dx}{\left[ \int_0^z P_s(x) \, dx \right]^2}.
\]

The net pair potential between two flat plates per unit area, \( E(z) / A \), is given by the sum of expressions (2.1) and (2.6). With the Derjaguin approximation we can now convert \( E(z) / A \) to \( E(h) \), the net pair potential between two spheres of diameter \( \sigma_1 \) and \( \sigma_2 \), and is given as [46]

\[
E(h) \approx \pi \left( \frac{\sigma_1 \sigma_2}{\sigma_1 + \sigma_2} \right) \int_h^\infty \frac{E(z)}{A} \, dz, \quad (2.7)
\]

for equal sized spheres \( \sigma_1 = \sigma_2 \)

\[
E(h) \approx \frac{\pi \sigma}{2} \int_h^\infty \frac{E(z)}{A} \, dz = \frac{\pi \sigma}{2} W(h). \quad (2.8)
\]

In all ensuing discussions, the binding strength, \( E_{XY} \), is defined minimum of \( E(h) \) for any two spheres, X and Y.
Example plots of the pair potential function as described by eqs. (2.1) – (2.8) are shown in Fig. 2.2 for several different values of $E_{xy}$. Note that the binding energy depends exponentially on the system temperature and free energy change for hybridization of the linker and the two grafted strands as shown in eq. (2.6), leading to very strong temperature dependence of the binding energy. This is in stark contrast to potentials representing atomic systems in which the binding energy is essentially independent of temperature. Due to this temperature dependence, the range for crystal formation is typically only about 0.5°C [11].

Figure 2.2: DNA-mediated pair potential for several different values of binding strength ($E_b$). Solid line - $E_b = 2.0k_B T$, short-dash line - $E_b = 4.0k_B T$, long dash line - $E_b = 6.0k_B T$. 

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2.2.2 Summary of Experimental Results for Binary Segregation in Solid-Solution Crystallization

An experimental realization of a binary colloidal system is described in ref. [59] in which solid-solution, close-packed crystals were grown and analyzed. In order to set the stage for the simulations described in this paper some basic considerations of the experimental findings are summarized here. In general, if the difference in strand sequence on the two sphere populations decreases the A-B bridge formation energy by \( \Delta(\Delta G) \) relative to an A-A bridge, then the sphere-sphere binding energies are related by

\[
\frac{E_{AA}}{E_{AB}} = e^{(\Delta \Delta G/k_B T)} = \alpha, \quad (2.9a)
\]

and

\[
\frac{E_{AA}}{E_{BB}} = \alpha^2. \quad (2.9b)
\]

This result predicts that particle segregation should be highly sensitive to small changes in hybridization free energy. For example, if \( \Delta(\Delta G) = 0.25k_B T \) and \( E_{AA} = 4k_B T \) then \( \alpha = 1.28 \), resulting in a binding energy difference of \( \Delta E = E_{AA} - E_{AB} = (1 - 1/\alpha) E_{AA} = 0.88k_B T \). Given that the typical free energy penalty for a single nucleotide mismatch is about 2 \( k_B T \) [83], the energetic cost of inserting one B sphere (with the engineered mismatch) into a close-packed (12-fold coordinated) host crystal of A spheres would be about \( 12\Delta E \approx 10k_B T \). This extremely large penalty
indicates that $B$ spheres should be completely excluded assuming that the system was able to grow at or near equilibrium conditions. In order to reduce the penalty for inserting a $B$ sphere and therefore allow a finite incorporation rate, mismatches were created on both $A$ and $B$ particles [57].

The extreme sensitivity of interfacial segregation to DNA hybridization energy was confirmed experimentally. Briefly, two suspensions were employed in which one contained GG and GA mismatches on the $A$ and $B$ particles, respectively, and had the smallest accessible $\Delta(\Delta G)_{GG/GA} \approx 0.22k_B T$, while a second contained GG and GT mismatches, leading to a larger $\Delta(\Delta G)_{GG/GT} \approx 1.25k_B T$. Following crystallization, the GG/GA system exhibited a substitution ratio of $0.092 \pm 0.009$ for crystallites grown from a suspension with 50:50 $A:B$ stoichiometry, and $0.0154 \pm 0.0025$ for crystallites from a 90:10 $A:B$ suspension. In both experiments, the segregation coefficient (defined as the ratio of the fraction of impurity $B$ particles in the crystal to that in the fluid) was consistent with the value $k_{seg} = 0.18 \pm 0.02$. As expected for the GG/GT case, with its larger $\Delta(\Delta G)$, no $B$ microspheres were observed in the grown crystals, which typically contained thousands of particles, implying that, for this case, $k_{seg} < 10^{-3}$.

While the values for the segregation coefficients obtained experimentally appear qualitatively to be in line with expectations, further analysis suggests that the process of crystallization may not correspond to a single, well-defined equilibrium one. Under full bulk equilibration, the ratio of probabilities of incorporating $A$ and $B$ particles into a growing close-packed crystal is given by

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\[ k_{\text{bulk}} = \exp(-12\Delta E / k_B T), \quad (2.10) \]

where the factor 12 represents the fact that a particle is fully coordinated within the crystal bulk. On the other hand, bulk equilibration generally is not possible in colloidal crystals because of the dense packing and it may be more reasonable to suppose that segregation is determined by interactions with somewhat fewer particles on the surface. We therefore define a quantity, \( N_{\text{eff}} \), which represents the number of crystallized surface particles with which an arriving particle interacts with before becoming permanently attached to the growing crystal. \( N_{\text{eff}} \) is a function of the growth kinetics as well as the interface structure at growth sites. Within this simple interpretation, eq. (2.10) can be generalized into the form

\[ k_{\text{seg}} = \exp(-N_{\text{eff}} \Delta E / k_B T). \quad (2.11) \]

For the GG/GA mismatch case, rearranging eq. (2.11) to solve for \( N_{\text{eff}} \) gives

\[ N_{\text{eff}} \equiv -\ln(k_{\text{seg}})/k_B T / \Delta E = 1.90 \pm 0.35. \]

Here, \( \Delta E \) was assumed to be approximately \( 1.0 k_B T \), which is a reasonable estimate for the experimental conditions in ref. [59].

The small value of \( N_{\text{eff}} \) obtained from the experiments suggests that particles arriving at the growing crystal surface are only equilibrated with respect to two surface particles before becoming locked into the crystal. In other words, the growth process has a rather low fidelity for compositional selection during growth. In the following sections, we seek to quantitatively explain these results, and in the process, develop a general
framework for understanding how interfacial equilibration occurs at the surface of growing colloidal crystals that are governed by short-ranged interactions.

2.3 Simulation Protocol

Matter can be modeled through a vast variety of simulation methods, as shown in Fig. 2.3. At the quantum level, electronic distributions are explicitly considered in formulating particle interactions, as in Density Functional Theory [42, 60]. At the atomic scale, empirically-derived interaction potentials, such as the Lennard-Jones potential [33], are used to calculate the properties of choice; either molecular dynamics (MD) or Monte Carlo (MC) simulations can be applied. Larger length and timescales can be accessed through coarse-graining of unimportant degrees-of-freedom; examples of such as mesoscale approaches (shown in Fig. 2.3) include Brownian Dynamics (BD) and Dissipative Particle Dynamics (DPD) [33]. For example, in BD, which is often applied in simulations of colloidal suspensions, degrees-of-freedom corresponding to the solvent molecules are only implicitly considered. Finally, in continuum simulations, particles are replaced by fields, and the system is generally represented by partial differential equations, such as modeling the stress-strain response of nanocrystalline nickel [110].
Figure 2.3: Molecular Simulation Scales. Simulation methods relevant to the study of colloids are outlined within the mesoscopic modeling block. The set of simulation methods that does not conserve the system’s momentum are called diffusive, while conservative methods are called hydrodynamic. SD: Stokesian Dynamics. DPD: Dissipative Particle Dynamics.

The simulation protocol is schematically shown in Fig. 2.4. Both Metropolis Monte Carlo (MMC) and Brownian dynamics (BD) simulations were performed to study the binary crystal growth process using the pair potentials described in Section 2.2.2. For both types of crystal growth simulations, a periodic cubic simulation cell containing 5,000 randomly distributed, non-overlapping particles [51, 53] at a prescribed volume fraction, $\phi$, (where $\phi ~ 0.1-0.4$) was allowed to relax to an average energy at a prescribed temperature and volume (constant NVT ensemble). For a given run, the
temperature was fixed at a value that provided the desired interaction well-depths according to the potential function specified in refs. [11, 59], so that $3.0k_B T < E_{AA} < 6.0k_B T$ and $0.4k_B T \leq \Delta E \leq 1.5k_B T$.

To ensure that the initial fluid configuration has no particle-particle overlap, we modified and combined the algorithms proposed in refs. [51, 53] for the construction of a simulation cell (of length $B$) with uniformly distributed particles. The details of our algorithm are as follows:

1. Randomly distribute $N$ particles of diameter, $\sigma$, within the simulation cube.
2. Find and list in ascending order distance between pair of particles, $d$. Particles can only belong to one pair. For every $d$, store the identity of particles comprising the pair. Set $d_M$ to equal the maximum distance between pairs.
3. Determine the minimum packing fraction, $c_m = N(\pi/6)(d_m/B)^3$, where $d_m$ is the minimum distance. If $d_m < \sigma$, spread apart symmetrically the pair of particles from $d_m$ to $\sigma + \delta$, where $\delta$ is very small tolerance. If $d_m > \sigma$, exit the algorithm.
4. For the $k$-th iteration of the algorithm, update $d_M^k$ by $d_{M}^{k+1} = d_{M}^{k} - v(c_{M}^{k} - c_{m}^{k})^a / N$, where $v$ and $a$ are the user specified rate of decrease and exponent of the algorithm.
5. Return to step 2. The process stops at the $l$-th iteration when $d_{M}^{l} < d_{m}^{l}$.

For all interaction strengths and system volume fractions considered in our study, a metastable fluid phase was obtained following relaxation of the initial random particle positions because of the large free energy barrier associated with crystal nucleation [32]. Once the fluid was equilibrated, a spherical close-packed (fcc) crystallite containing 30-150 particles was inserted into the center of the equilibrated fluid (replacing an equal number of fluid particles). The system was allowed to further relax while keeping the seed particles fixed. When the surrounding fluid was equilibrated with the fixed seed, the
seed particles were released and the entire system was allowed to further evolve without constraints. Using this initialization procedure, the nucleation barrier against crystallization was circumvented allowing us to focus on a single growing crystallite. During the course of each simulation, particles were periodically identified as solid or fluid and the cluster size distribution was noted. Solid particles were identified using a local bond order analysis first outlined by [96] and later applied by Frenkel and co-workers [7, 98].

**Figure 2.4:** Simulation protocol for evaluating crystal growth. The protocol is outlined as follows: (1) equilibration of desired fluid [51, 53], (2) seeding the equilibrated fluid, (3) re-equilibrate the fluid and seed system, with static seed [51, 53], and (4) release the seed and evolve the seeded system [7, 98].
2.3.1 Monte Carlo and Brownian Dynamics Simulation Details

As noted above, both MMC and BD simulations were used to study colloidal crystallization. We discuss the connections between the two simulations techniques later; here we present briefly the salient details for each. Further details are provided in Appendix A. We employed standard MMC with a Verlet neighbor list implementation [3]. Individual Monte Carlo moves were performed by displacing randomly selected particles with a uniformly distributed random vector with maximum magnitude, $r_d \max$, in each spatial dimension. Move attempts were accepted and rejected according to the standard Metropolis criterion. Particle assignment to solid and fluid was performed every 100 moves-per-particle, or sweeps.

The BD simulations were performed using the algorithm of van Gunsteren and Berendsen [36], which numerically integrates the Langevin equation

$$m_i \dot{v}_i(t) = - m_i \gamma_i v_i + F_i + R_i,$$

(2.12)

where $\gamma_i$, $v_i$ and $F_i$ are the frictional (damping) coefficient, velocity and systematic force acting on the $i^{th}$ colloid, respectively. $R_i$ represents a random, stationary stochastic force acting on particle $i$ that arises from interactions with the solvent molecules. Hydrodynamic interactions between particles were neglected in all BD simulations.

Note that the stochastic force, $R(t)$, is assumed constant over the integration interval, $\Delta t$, and therefore the correlation time for $R(t)$ is $O(\Delta t)$. Thus, in order to
generate the required stationary Markovian process during the numerical integration of
the Langevin equation, the constraint, $\Delta t \ll \gamma^{-1}$, must be obeyed, setting a limit on the
size of the time step that can be employed in the BD simulations (in addition to that
imposed by the accuracy of any given numerical integration scheme). Finally, we note
that in the limit $\gamma \equiv 3\pi \eta \sigma \to 0$, the BD algorithm in ref. [36] can be simplified to the
Verlet molecular dynamics algorithm [3], where the implicit solvent viscosity is now
$\eta \sim 0$ and purely inertial dynamics are present [36].

2.3.2 Identifying Solid and Fluid Particles

One of the most important aspects in the study of crystal nucleation and growth is a
robust metric for identifying particles as “solid” and “fluid”. In the subsequent
simulations, a cluster of size $n$ is identified by a local bond order analysis based on
spherical harmonics first outlined by [96] and later successfully applied by Frenkel and
coworkers [7] to colloidal suspensions. We first associate the spherical harmonics with
neighbors of each particle and compute

$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{r}_{ij}), \quad (2.13)$$

where $i$ is the $i$-th particle. $N_b$ is number of neighbors within a $r_q$ distance around $i$. $r_q$ is
selected such that $N_b$ contains only the first nearest neighbors for the face-centered cubic
(fcc), hexagonal close packed (hcp) and random hexagonal close packed (rhcp) lattices.

For the body-centered cubic (bcc) lattice, $r_q$ is selected such that $N_b$ contains the first and second nearest neighbors. $Y_{lm}$ is the spherical harmonic function. $\hat{r}_{ij}$ is the unit vector between particles $i$ and $j$. The $(2l + 1)$ components of $q_{lm}$ forms a vector, $\mathbf{q}_l$. The rotationally invariant bond-order parameters are then defined as

$$q_l(i) = \left( \frac{4\pi}{2l + 1} \sum_{m=-l}^{l} |q_{lm}(i)|^2 \right)^{1/2}, \quad (2.14a)$$

and

$$\hat{w}_l(i) = \frac{w_l(i)}{\left( \sum_{m=-l}^{l} |q_{lm}(i)|^2 \right)^{3/2}}, \quad (2.14b)$$

with

$$w_l(i) = \sum_{m_1, m_2, m_3} \left( \begin{array}{ccc} l & l & l \\ m_1 & m_2 & m_3 \end{array} \right) q_{lm_1}(i)q_{lm_2}(i)q_{lm_3}(i). \quad (2.14c)$$

The term in brackets in the last expression is the Wigner-3j symbol. These even-$l$ rotationally invariant bond-order parameters have a particular advantage: the identification of a cluster is independent on its orientation within space. The first nonzero averages occur for $l = 4$ for systems with cubic symmetry and for $l = 6$ in icosahedrally oriented systems [96]. Typical distribution functions of the local bond-order parameters ($q_4$, $q_6$, $\hat{w}_4$ and $\hat{w}_6$) calculated in a Monte Carlo simulation of hard-spheres (HS) near coexistence, where the liquid and solid phases are equally stable, are
shown in Fig. 2.5. Here, the distributions of the \( l = 4 \) bond-order parameters overlap significantly. For the \( l = 6 \) distributions, the bond-order parameter for solid phases shift more to higher values, which indicates higher bond correlations between adjacent particles within the solid phase. Also, the \( q_6 \) distribution function has further separation between the solid phases.

![Distribution functions of the local bond-order parameters: \( q_4, q_6, \hat{w}_4 \) and \( \hat{w}_6 \) from Monte Carlo simulations in a hard-sphere system [7].](image)

**Figure 2.5:** Distribution functions of the local bond-order parameters: \( q_4, q_6, \hat{w}_4 \) and \( \hat{w}_6 \) from Monte Carlo simulations in a hard-sphere system [7].

To further enhance this separation, the \( \mathbf{q}_6(i) \) vector is dotted with its \( j \) neighbors (\( \mathbf{q}_6(i)\mathbf{q}_6(j) \)), and the \( \mathbf{q}_6(i)\mathbf{q}_6(j) \) solid threshold value is defined as 20. Particles with a \( \mathbf{q}_6(i)\mathbf{q}_6(j) \) value greater than the solid threshold are deemed solid-like (Fig. 2.6 a). However, a particle is identified as a solid particle only if it is connected to at least 7 other solid-like particles. This value is called the connection threshold and is shown in Fig. 2.6 b. Finally, solid particles that are within 2 diameters of each other are identified as belonging to the same cluster [97].
Figure 2.6: The identification of solid and fluid particles. a, the distribution of the $q_6q_6$ quantity for a supersaturated hard-sphere system, where the arrow indicates the solid threshold. b, the distribution of the number of connection, where the arrow indicates the connection threshold. A particle is identified as solid if and only if its distribution functions are larger than both the solid and connection thresholds.

2.4 Results and Discussion

2.4.1 Simulating Crystal Growth “Dynamics” with Monte Carlo

Generally, crystal growth from a surrounding supersaturated fluid proceeds by diffusion to the crystal surface, followed by the dynamic processes of particle attachment and detachment from the surface. The overall crystal growth process can be characterized by two timescales: the timescale of the crystal growth and the diffusion timescale to the
crystal front. The growth timescale for a monolayer of crystal is then given by

\[ \tau_{\text{growth}} = \frac{\sigma}{dr/ds}, \]

where \( dr/ds \) is the radial growth rate, \( s \) is the number of MMC sweeps, and \( \sigma \) the particle diameter. Similarly, if the radial diffusion length scale within the fluid surrounding the crystal is assumed to be on the order of a particle diameter, \( \tau_{\text{diff}} = \frac{\sigma^2}{D} \), where \( D \) is the bulk fluid diffusion coefficient. A dimensionless crystal growth rate, \( \Gamma_D \), can then be defined as the ratio of \( \tau_{\text{diff}} \) to \( \tau_{\text{growth}} \) i.e.

\[
\Gamma_D \equiv \frac{\tau_{\text{diff}}}{\tau_{\text{growth}}} = \frac{(dr/\sigma)\sigma}{D}. \tag{2.15}
\]

Note that the dimensionless quantity \( \Gamma_D \) is explicitly independent of MMC sweeps and therefore can be compared directly to an equivalent quantity obtained from BD simulations or experimental measurements. This will be addressed in detail in a later section.

The radial crystal growth rate, and therefore \( \Gamma_D \), can be readily shown to be constant under conditions of constant particle arrival flux, \( J(\phi,E_b) \), which prevail when the fluid volume fraction, \( \phi \), is approximately constant. The arrival rate of particles to the crystal surface is then given by

\[
dn/ds = \beta n^{2/3}J(\phi,E_b), \tag{2.16}
\]
where $\beta$ is a geometric factor that depends on the crystallite shape. Under the assumption of spherical crystallite geometry, the radius of a growing crystal is defined as 

$$r = \left(\frac{\sigma}{2}\right) n^{1/3} \phi_{\text{cr}}^{-1/3},$$

where $\phi_{\text{cr}}$ is the volume fraction of the crystal, and $n$ is the number of colloids in the growing crystallite. Using this expression for the radius in eq. (2.16) gives

$$\frac{dr}{ds} = \frac{(\sigma / 6) \beta J(\phi, E_b) \phi_{\text{cr}}^{-1/3}}{A}, \quad (2.17)$$

where $A$ is a constant if the arrival flux is constant. As shown in Fig. 2.7, the radial growth rate for a single-component crystal obtained from MMC simulations with several different values for overall volume fraction, $\phi$ and particle binding energy, $E_b$, indeed exhibits the expected linear behavior after a short initial transient. Note that at long simulation times, the fluid density becomes appreciably depleted which leads to a continuous reduction in the crystal growth rate.
2.4.2 MMC Simulation of Binary Solid-Solution Colloidal Crystals

Binary crystallization was simulated using the protocol described in the previous section. As mentioned earlier, the binary systems considered here are constructed so that \( E_{AA} > E_{AB} > E_{BB} \). The properties of the A particles were used to define \( \Gamma_D \) so that \( \Gamma_D = (dr/ds)\sigma/D_A \), where \( D_A \) is the bulk fluid diffusivity of A particles [59]. All binary MMC simulations were equilibrated using pure A seeds containing 150 particles arranged in an fcc configuration and initialized with a fixed composition of particles within the overall simulation. In order to remove any bias imposed by this choice of initial seed
composition, growth rate data was collected after about one monolayer of particles had been added to the seed.

The binary segregation coefficient, $k_{\text{seg}}$, defined in Section 2.2.2 was computed across a large range of $\Gamma_D$ values. To access different $\Gamma_D$ values in simulation, a sequence of MMC runs were performed using different values of $E_{AA} (3.75k_B T - 5.0k_B T)$, $E_{AB} (0.4k_B T \leq \Delta E \leq 1.5k_B T)$, overall system volume fraction $(0.25 < \phi < 0.4)$ and $r_{d,\text{max}} (0.015 \sigma < r_{d,\text{max}} < 0.06 \sigma)$. Our base case particle size was $\sigma = 0.98 \mu m$, corresponding to the experimental system described in Section 2.2.2. For each value of segregation coefficient, the effective number of bonds with which an arriving particle equilibrates was calculated on the basis of the theory presented in Section 2.2.2:

$$N_{\text{eff}} = \frac{-k_BT \ln k_{\text{seg}}}{\Delta E}.$$  

(2.18)

A plot of $N_{\text{eff}}$ as a function of $\Gamma_D$ for $\sigma = 0.98 \mu m$ particles reveals a single master curve as shown in Fig. 2.8, regardless of what parameters values were used to generated a particular value of $\Gamma_D$. This result suggests that the segregation behavior is completely controlled by a competition between the growth rate and a process (or processes) whose rate is proportional to bulk-like diffusion. Under slower growth conditions (relative to bulk diffusion), $\Gamma_D < 0.2$, non-stoichiometric substitution is observed in which $B$ particles are actively rejected relative to $A$ particles at the growing crystal front. In the interval,
0.05 < \Gamma_D < 0.2 \), \( N_{\text{eff}} \) rises rapidly as \( \Gamma_D \) decreases until reaching a plateau at \( N_{\text{eff}} \sim 2 \). This plateau extends across approximately one decade down to \( \Gamma_D \sim 0.003 \), at which point \( N_{\text{eff}} \) once again rises rapidly to a value of approximately 3. Example configurations of grown crystallites are shown in Fig. 2.9 for various values of \( \Gamma_D \).

Overall, our simulation results suggest that the segregation process is governed by staircase-like hierarchy corresponding to different integer values of \( N_{\text{eff}} \) as \( \Gamma_D \) is varied. At high values of \( \Gamma_D \) (above \( \sim 0.2 \)) \( N_{\text{eff}} \sim 0 \) indicating fully non-equilibrium, stoichiometric growth (i.e. no rejection of particles by the growing crystal front). Note that although the crystal is fully stoichiometric (i.e. no segregation relative to the fluid composition) under these conditions, the crystal remains morphologically perfect, with no structural defect formation apparent as shown in Fig. 2.9 b. The onset of the dendritic shape instability [52, 75, 76], corresponding to the onset of morphological disturbances, is seen by \( \Gamma_D \sim 0.7 \), Fig. 2.9 c.

Also shown in Fig. 2.8 is a data point generated from the experiments discussed in Section 2.2. The \( \Gamma_D \) value corresponding to the experimental conditions (\( \Gamma_D \sim 0.01 \)) was calculated by directly measuring the crystal growth rate (\( \sim 3 \times 10^{-4} \text{ \mu m/sec} \)) and correcting the bulk fluid diffusion coefficient to account for lubrication effects (\( D_A \sim 0.03 \text{ \mu m}^2/\text{sec} \)).

The latter arise because of hydrodynamic interactions between particles at low separation and are neglected in the MMC simulations. There is very good agreement between this experimental data point and the simulation predictions, although further studies will be required to fully validate the simulation results. Note that the careful control of crystal
growth rate required to systematically probe other values of \( \Gamma_D \) with experiments is rather challenging.

**Figure 2.8:** Segregation behavior during binary crystallization of a solid-solution as a function of scaled crystal growth rate (\( \Gamma_D \)). Open circles – MMC simulations for \( \sigma = 0.98 \mu m \); filled square – experimental measurement. Dashed line is a guide to the eye.
Figure 2.9: Snapshots showing MCM files of grown crystals. Crystals are grown at low values of $\Gamma_D$ ($\sim 0.002$) (a) and high values of $\Gamma_D$ ($\sim 0$) (b) and (c). Simulation conditions: (a), $\phi=0.3$, $E_{AA}=3.75k_BT$ and $\Delta E=1.25k_BT$; (b), $\phi=0.25$, $E_{AA}=6.0k_BT$ and $\Delta E=0.4k_BT$; and (c), $\phi=0.35$, $E_{AA}=6.0k_BT$ and $\Delta E=0.4k_BT$. All simulations contained particles with $\sigma=0.98\mu m$ at 50:50 $A:B$ stoichiometry.

While the discrete nature of the segregation process as a function of scaled growth rate is qualitatively understood in terms of an effective number of bonds controlling particle detachment, a more quantitative picture can be formulated. Mechanistically, the timescale associated with detaching a particle from the crystallite surface can be decomposed into two contributions: first, the bonds between the particle and the surface must be broken, and second, the particle has to diffuse sufficiently far away from the crystallite so that no memory of its excursion to the crystal is retained. The latter condition ensures that no correlation exists between a detachment and a subsequent attachment event. A simple model for these two sequential sub-processes can be expressed by

$$\tau_{\text{diss}}^N = \frac{L_w^2}{D_A} \exp \left( \frac{NE_{bb}^{AA}}{k_BT} \right) + \frac{(2\sigma)^2}{D_A},$$

(2.19)
where $L_w$ is the interaction length for the pair potential and $N$ is the number of bonds that must be broken to free the particle under consideration. The bond-breaking timescale (1st term in eq. (2.19)) is assumed to be determined by the breaking of the strongest bonds, i.e. those between two $A$ particles. The diffusion length scale employed in the second term in eq. (2.19), $2\sigma$, is approximately equal to the thickness over which fluid ordering is observed due to the proximity of the crystal. The hierarchy of different detachment processes represented by eq. (2.19) is shown schematically in Fig. 2.10 for the first three.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.10.png}
\caption{Schematic representation of different particle dissociation processes on the surface of a colloidal crystal.}
\end{figure}

Using eq. (2.19), a sequence of rescaled growth rates then can be defined as

$$\Gamma_N \equiv \frac{\tau_{\text{dis}}^N}{\tau_{\text{growth}}}, \quad (2.20)$$

\[
\begin{align*}
\text{N=1} & \quad \text{N=2} & \quad \text{N=3} \\
\end{align*}
\]

each of which compares the relative rates of crystal growth to a particular escape process defined by the number of bonds that must be broken to enable particle detachment from the crystal. In Fig. 2.11, the value of $N_{\text{eff}}$ is plotted against $\Gamma_2$, $\Gamma_3$, and $\Gamma_4$. Interestingly, the step transitions, $N_{\text{eff}} (\Gamma_2) = 1 \rightarrow 2$ and $N_{\text{eff}} (\Gamma_3) = 2 \rightarrow 3$, are now aligned.
at about $\Gamma_N \sim 1$. In other words, each step transition occurs when the corresponding $\Gamma_N$ approaches unity. For example, as $\Gamma_2$ increases towards unity, the rate of the dissociation processes associated with the breakage of two bonds becomes comparable to the crystal growth rate, and equilibration of this process is no longer possible. At this point, $N_{\text{eff}}(\Gamma_2)$ is expected to decrease to a value below two. Assuming that the faster one-bond dissociation process is still equilibrated, the observed $N_{\text{eff}}$ value would be about one, until $N_{\text{eff}}(\Gamma_1)$ becomes $\sim 1$, at which point a further decrease in $N_{\text{eff}}$ would occur. Similar considerations apply for the entire hierarchy of dissociation processes. The dashed line representing the transition $N_{\text{eff}}(\Gamma_4) = 3 \rightarrow 4$ shown in Fig. 2.11 is not based on actual data but represents the expected behaviour from the present mechanistic model. Unfortunately, accessing simulation conditions corresponding to $N_{\text{eff}} = 4$ is simply too computationally expensive because of the extremely slow growth rates required.
Figure 2.11: $N_{\text{eff}}$ as a function of $\Gamma_2$ (green squares), $\Gamma_3$ (red circles) and $\Gamma_4$ (cyan diamonds). Shaded region represents transition area where $\Gamma_N \sim 1$ for all $N$. Data shown corresponds to $\sigma = 0.98 \mu m$ particles.

2.4.3 Connections to Segregation in Atomic Systems

In this section, the results from this work are compared to typical segregation behavior observed in atomic systems. Although the pair potential derived for the DNA-mediated system is qualitatively similar to that for simple atomic systems (e.g. a Lennard-Jones model for noble gases), key differences exist such as the interaction range and the shape of the soft-core repulsion. The former, in particular, is well known to drastically alter the
phase diagram relative to atomic systems [32]. In order to draw a quantitative comparison between segregation behavior in our colloidal system and a typical atomistic one we consider the work of Beatty and Jackson [10, 48] who define a rescaled crystal growth rate, $\beta$, as [48]

$$\beta = \frac{u\tau_C}{\sqrt{D\tau_C}}, \quad (2.21)$$

where $u$ is the crystal growth rate, $\tau_C$ is the average time it takes for a particle to join the crystal, which is approximated here as the time required to diffusive through the ordered fluid layer near the crystal surface, and $D$ is the diffusion coefficient of the bulk fluid. The parameter $\beta$ can be connected to $\Gamma_D$ by noting that $u \sim dr/ds$ and $\tau_C \sim \sigma^2 / D$ so that $\beta \sim \Gamma_D$.

Our data is plotted along with the results of Beatty and Jackson for the tin-silicon binary system [10] in Fig. 2.12. In order to define corresponding $N_{\text{eff}}$ values for the atomistic data, we assume that the value of the equilibrium segregation coefficient used in ref. [10] ($k_{\text{seg}}^{\text{eq}} = 0.023$) corresponds to equilibrating the maximum possible number of bonds on the growing crystal surface. The latter value is taken to be approximately 4 for the growth of diamond-like crystals, which assumes that bulk reorganization is operational under equilibrium growth conditions. Applying eq. (2.18) then gives an estimate for the parameter, $\Delta E \sim k_B T$, which was used plot the data from ref. [10] in Fig. 2.12. Notably, the atomistic segregation coefficient does not exhibit the stepped behavior.
predicted for the colloidal system although similar values of $N_{\text{eff}}$ are apparent for equivalent scaled growth rates. The short-ranged nature of the colloidal interactions (at least for the particle sizes used in the present study) is therefore directly attributable to the steps in the $N_{\text{eff}}$ curve. In the atomistic model, longer-ranged interactions effectively smear out the steps because approaching particles can form multiple bonds over a broad range of positions, whereas only very specific sites allow for multiple bond formation in the colloidal case.

![Figure 2.12: Comparison of the binary colloidal (open circles) to atomistic (filled diamonds) [10] segregation behavior. The atomistic segregation behavior is continuous compared to the kinetically limited integer segregation behavior of the binary macromolecule. Solid line is a polynomial fit to the atomistic data.](image)

We bridge our results for micron-sized colloidal particles to that for atomic systems by considering smaller colloidal particles. Additional binary crystallization
simulations were performed with smaller microspheres \((\sigma = 0.3\, \mu m \text{ and } 0.1\, \mu m)\), but with the same DNA oligomers used in the original system. Plots of \(N_{\text{eff}}\) against scaled growth rate for these two additional systems are shown in Fig. 2.13, along with the prior results for \(\sigma = 0.98\, \mu m\). At \(\sigma = 0.3\, \mu m\), the overall segregation is observed to still be somewhat stepped in nature but the steps between the integer values of \(N_{\text{eff}}\) are now more diffuse, particularly in the region where \(0 \leq N_{\text{eff}} \leq 2\). The effect is even more pronounced for \(0.1\, \mu m\) diameter particles, although computational limitations prevent us from accessing \(N_{\text{eff}}\) values above 2. Nevertheless, for the \(0.1\, \mu m\) case, the evolution of the segregation behaviour already appears to closely resemble that of an atomistic system. Note that for \(0.1\, \mu m\) diameter particles, the ratio of the interaction range to the particle diameter, \(L_w / \sigma\), is still quite small (~0.3).

**Figure 2.13:** Segregation behavior as a function of colloid size for a fixed-range inter-particle interaction potential. Dashed-line and open circles – base-case \(\sigma = 0.98\, \mu m\); red
diamonds – $\sigma = 0.3 \mu m$; green squares – $\sigma = 0.1 \mu m$. Solid line represents a fit to the atomistic data in ref. [10] for comparison.

2.5 Analysis of MMC Simulation of Brownian Dynamics

In the final section of this paper, we discuss the theoretical basis for connecting our MMC results to those from Brownian dynamics (BD) simulations. The theory for this connection is well established and proceeds via the Fokker-Planck equation (FPE) [56, 89]. In fact, the literature is replete with examples that demonstrate the applicability of MMC for simulating overdamped dynamics with applications to micromagnets [17], classical magnetic moments [77], protein chains [99], and vacancy cluster diffusion [55]. In this section, we summarize the basic elements of this theory and use it to analyze the validity of using MMC to perform the studies presented in the preceding sections. In particular we show that single-move MMC can offer significant computational advantages relative to BD simulations when applied to crystallization problems.

The temporal evolution of $P(X,t)$, the probability of a Markovian system residing in a state $X$ at time $t$, is given by the Master equation

$$\frac{\partial P(X,t)}{\partial t} = \int \psi (X';\Delta X) P(X',t)d(\Delta X) - \int \psi (X;\Delta X) P(X,t)d(\Delta X), \quad (2.22)$$
where $\psi(X;\Delta X)$ is the transition rate over a small but finite time interval, $\Delta t$, and $\Delta X \equiv X - X'$. For small $\Delta X$, the Master equation can be approximated by a Fokker-Planck equation of the form [54, 82]

$$\frac{\partial P(X,t)}{\partial t} \approx -\frac{\partial}{\partial X}[A(X)P(X,t)] + \frac{1}{2} \frac{\partial^2}{\partial X^2}[B(X)P(X,t)], \quad (2.23)$$

where

$$A(X) \equiv \int_{-\infty}^{\infty} (\Delta X) \psi(X;\Delta X) d(\Delta X) = \frac{\langle \Delta X \rangle}{\Delta t}, \quad (2.24)$$

and

$$B(X) \equiv \int_{-\infty}^{\infty} (\Delta X)^2 \psi(X;\Delta X) d(\Delta X) = \frac{\langle (\Delta X)^2 \rangle}{\Delta t}, \quad (2.25)$$

are the drift and diffusion coefficients, respectively. Following Kikuchi et al. [56], the drift and diffusion coefficients for the Metropolis Monte Carlo "process" can be derived by direct substitution of the Metropolis criterion into eqs. (2.24) and (2.25). For a proposed move in a one-dimensional system, the change in potential energy is

$$\Delta E = \frac{\partial E}{\partial X} \Delta X = \frac{\partial E}{\partial X} (rd_{\text{max}} \xi),$$

where $rd_{\text{max}}$ is the maximum displacement of the particle and $\xi$ is a uniform random number in the interval [-1,1]. The mean displacement and mean square-displacement over a number of MMC moves are given by [56]

$$\langle \Delta X \rangle = \sum_{\Delta X > 0} \frac{1}{Z} \Delta X + \sum_{\Delta X < 0} \frac{1}{Z} \exp\left(-\frac{1}{k_B T} \frac{\partial E}{\partial X} \Delta X\right) \Delta X, \quad (2.26)$$
\[
\langle (\Delta X)^2 \rangle = \sum_{\Delta X > 0} \frac{1}{Z} (\Delta X)^2 + \sum_{\Delta X < 0} \frac{1}{Z} \exp \left( -\frac{1}{k_B T} \frac{\partial E}{\partial X} \Delta X \right) (\Delta X)^2,
\]
respectively, where \( Z \) is a normalization factor that denotes the total finite number of possible states in a discretized system.

For sufficiently small \( \Delta X \), the exponential terms in eqs. (2.26) and (2.27) can be expanded in powers of \( \alpha = \frac{1}{k_B T} \frac{\partial E}{\partial X} \Delta X \). Truncating the expansion to third order in \( \alpha \) leads to the following expressions for the FPE drift and diffusion coefficients (see Appendix B for derivation):

\[
A(X) = -\frac{1}{k_B T} \frac{\partial E}{\partial X} \left( \frac{r d_{\text{max}}}{\Delta t} \right)^2 + \left( \frac{1}{k_B T} \frac{\partial E}{\partial X} \right)^2 \left( \frac{r d_{\text{max}}}{\Delta t} \right)^3 + O\left( \frac{r d_{\text{max}}}{\Delta t} \right)^4,
\]

\[
B(X) = \frac{(r d_{\text{max}})^2}{3 \Delta t} - \frac{1}{k_B T} \frac{\partial E}{\partial X} \left( \frac{r d_{\text{max}}}{\Delta t} \right)^3 + O\left( \frac{r d_{\text{max}}}{\Delta t} \right)^4.
\]

Consider first the situation where \( \alpha \ll 1 \) and the first term in the expansion above is dominant. Under these conditions, the Fokker-Planck equation, eq. (2.23), suggests that \( B(X) = 2D \), or \( D = \left( \frac{r d_{\text{max}}}{\Delta t} \right)^2 / 6 \Delta t \), which then implies that the drift coefficient is given by

\[
A(X) \approx -\frac{D}{k_B T} \left( \frac{\partial E}{\partial X} \right) = -\frac{\partial E}{\gamma} \left( \frac{\partial E}{\partial X} \right),
\]
where the second equality in eq. (2.28) makes use of the Einstein relation \( D/k_BT = 1/\gamma \).

The result in eq. (2.29) is identical to the drift resulting from overdamped (diffusive) Langevin dynamics (with no hydrodynamic interactions present) as described in ref. [54],

\[
\gamma \frac{dX}{dt} = -\frac{dE}{dX} + R(t). \tag{2.31}
\]

In other words, for sufficiently small \( \Delta X = r d_{\text{max}} \xi \), the dynamics generated by MMC and solution of the inertialess Langevin equations are identical to within an underdetermined conversion factor between the number of MMC moves and time. Note that this equivalence is established on the scale of many MMC moves, i.e. long enough to establish the averages denoted in eqs. (2.24) – (2.27).

As \( r d_{\text{max}} \) (and thus \( \Delta X \)) is increased, the convergence rate of the expansion applied to eqs. (2.26) and (2.27) is reduced and additional terms become significant. Including additional terms within the expansions in eq. (2.28) and (2.29) implies that the drift and diffusion coefficients no longer are consistent with Langevin dynamics [41] [111]. However, the ratio of the \( (r d_{\text{max}})^3 \) term to the \( (r d_{\text{max}})^2 \) term (in either eq. (2.28) or (2.29)) gives a criterion for establishing the validity of MMC simulations of dynamical trajectories:

\[
K \equiv \frac{3 \partial E r d_{\text{max}}}{8 \partial X k_BT} \ll 1. \tag{2.32}
\]
We validated the criterion in eq. (2.32), by performing MMC simulations of cluster center-of-mass diffusion for isolated tetramers. It is well known that in the absence of hydrodynamic interactions, the Brownian diffusivity for a cluster of \( n \) particles is given by

\[
\frac{D_{CM}}{D_{MONOMER}} = n^{-3/d},
\]  

(2.33)

where \( CM \) refers to the center-of-mass of the \( n \)-particle cluster and \( d \) is the dimension of the simulated system \([55, 106]\). Shown in Fig. 2.14 is a plot of the cluster diffusivity scaled by the monomer diffusivity as a function of \( K \) for tetrahedrally configured tetramers bound by the DNA potential used in the previous sections (\( \sigma = 0.98 \mu m \)). The value of \( K \) was obtained by averaging the gradient of the potential energy (calculated numerically as \( \Delta E / \Delta X \) for each MMC move). The deviation from the expected Brownian behavior (dashed line) initiates as \( K \sim 0.01 \pm 0.1 \) and becomes progressively worse with increasing \( K \), indicating that the criterion in eq. (2.32) is in fact the relevant one, at least for cluster diffusion. Notably, cluster diffusion is completely arrested for \( K \) values approaching unity. Also shown in Fig. 2.14 are tetramer diffusion results for the bead-spring interaction model example employed in ref. [56], which exhibits almost identical behavior.
Figure 2.14: Center-of-mass diffusion as a function of $K$ for single (tetrahedrally configured) tetramer clusters, scaled by the monomer diffusivity. Open symbols – bead-spring model [56]; filled symbols – DNA-mediated interactions. Horizontal dashed line corresponds to theoretical Brownian center-of-mass diffusivity for tetramer, scaled by monomer diffusivity.

Next, the averaged $K$ values were calculated for the crystal growth MMC simulations presented earlier; these are shown in Fig. 2.15 for the $\sigma = 0.98 \mu m$ data, along with the corresponding $N_{eff}$ vs. $\Gamma_D$ data. The resulting $K$ values are distributed tightly in the range $0.2 < K < 0.5$, with some even higher instances. Clearly, the MMC simulations were generally performed under conditions that do not satisfy the criterion in eq. (2.32). On the other hand, also shown in Fig. 2.15 are the $N_{eff}$ vs. $\Gamma_D$ data generated by BD and MD simulations for $\sigma = 0.98 \mu m$ microspheres. Note that the introduction of a scaled growth rate, $\Gamma_D$, allows for a direct comparison between the results of the two simulation
methods because the MMC sweep/time factor cancels out in the definition of $\Gamma_D$. In the BD case, the friction coefficient, as well as binding energies and system volume fractions, was used to generate a range of $\Gamma_D$ values, while only the latter were adjustable in the purely inertial MD case. Interestingly, the BD and MD data is statistically indistinguishable from the MMC data, although it was not possible to access very low values of $\Gamma_D$ ($<10^{-2}$) with either method. Moreover, the BD and MD runs at equivalent values of $\Gamma_D$ were consistently slower than the MMC runs by up to a factor of 10 – 20, making the MMC simulations an attractive alternative.

**Figure 2.15:** Comparison of segregation behavior as a function of scaled growth rate during binary crystallization obtained from MMC (open circles), BD (open squares), and MD (open diamonds). Filled circles represent the K value for each of the MMC data points. All runs correspond to $\sigma=0.98 \mu m$. 

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The agreement between the BD, MD, and MMC data is at first somewhat surprising given the violation of the criterion in eq. (2.32). To understand the apparent robustness of the master curve in Fig. 2.15, we consider the effect of varying the parameter \( r_{d_{\text{max}}} \) on the basic processes taking place within the simulations: bulk fluid diffusion and crystal growth. Shown in Fig. 2.16 are plots of the dependence of the bulk fluid self-diffusivity, the crystal growth rate, and the resulting value of \( \Gamma_D \) on \( r_{d_{\text{max}}} \) for three different binding energies in a single-component system. The bulk fluid diffusivity (defined in terms of MMC sweeps) in Fig. 2.16 a increases with \( r_{d_{\text{max}}} \), but slower than the expected \((r_{d_{\text{max}}})^2\) scaling for the range considered (dashed line). The deviation arises because of the high particle volume fraction (30%) which naturally reduces the self-diffusivity, and the fact that over much of the \( r_{d_{\text{max}}} \) range considered, the small clusters that exist in the bulk fluid (in equilibrium with monomers) are artificially arrested due to increasing move rejection rate by the MMC method as shown in Fig. 2.14. Note that the latter effect increases with increasing binding energy as expected from eq. (2.32).

The crystal growth rate exhibits a more complex dependence on \( r_{d_{\text{max}}} \), in which it first increases, and then decreases, for all binding energies. In the following, we establish a quantitative framework for analyzing these results by estimating the growth rate under purely diffusion-limited conditions. Assuming a spherically symmetric crystal and diffusion-limited growth conditions, the growth rate of a crystal is given by

\[
\frac{dn}{ds} = \frac{DC_0}{\sigma} A_c, \quad (2.34)
\]
where, $C_0$ is the far-field (number) concentration of particles, $A_c$ is the crystal surface area, $n$ is the number of particles in the crystal, $s$ is the number of MMC sweeps. In eq. (2.34), it was assumed that the length-scale of the diffusion profile around the growing cluster is of order $\sigma$, and the equilibrium fluid particle concentration at the cluster surface is small relative to $C_0$, consistent with a continuum interpretation of diffusion-limited growth [23]. Noting that $r_c = (n / \phi_c)^{1/3} \sigma / 2$, where $r_c$ is the crystal radius and $\phi_c$ is the crystal volume fraction, eq. (2.34) can be rewritten as

$$
\frac{dr_c}{ds} = \frac{\pi \sigma^2}{6 \phi_c} D C_0 \sim \frac{\phi}{\phi_c \sigma} D .
$$

(2.35)

In other words, under diffusion-limited conditions, the radial growth rate is approximately of order the diffusion coefficient and scales as $(r_{\text{max}} \sigma)^2$. Equation (2.35) directly leads to the conclusion that

$$
\Gamma_D = \frac{\phi}{\phi_c} ,
$$

(2.36)

i.e. $\Gamma_D$ is a constant of order unity under diffusion-limited growth conditions. Returning to Fig. 2.16 b, the actual growth rate observed for different binding energies is seen to diverge away from the diffusion-limited behavior (dashed line) with increasing $r_{\text{max}}\sigma$, and actually decreasing for $r_{\text{max}} \sigma > 0.05$.$\sigma$. This decrease is readily attributable to the increasing fraction of particle attachment moves that are rejected by the MMC criterion. The combination of the effects shown in Fig. 2.16 a, b lead directly to the results in Fig.
2.16 c, whereby the simulated values of $\Gamma_D$ are seen to approach the diffusion-limited value as $rd_{\text{max}}$ decreases.

The observations in Fig. 2.16 suggest an explanation for the robustness of the binary segregation behavior in Fig. 2.15, and more generally for the crystal growth process considered in this work. Given the absence of any specific energy barrier for particle attachment at the growing crystallite surface, we would expect that an overdamped, diffusion-dominated system (such as MMC) would predict that the crystal growth process operates in the diffusion-limited regime. This would indeed be the result for MMC simulations operating at very small $rd_{\text{max}}$, as suggested by Fig. 2.16 c. As $rd_{\text{max}}$ is increased, deviation from diffusion-limited conditions arises because the increasing move rejection rate (i.e. the violation of the criterion in eq. (2.32)) affects the bulk fluid self-diffusivity and the particle attachment/detachment processes at the crystal surface in different ways. The fact that the crystal growth rate is affected more strongly than the bulk self-diffusivity creates conditions that are akin to the presence of an attachment barrier at the crystal surface, i.e. these effects could be interpreted in terms of a surface reaction limitation. The practical implication is that a larger range of dimensionless growth rates, $\Gamma_D$, can be accessed by varying the value of $rd_{\text{max}}$.

Similar arguments can be made regarding the BD and MD results. In order to access lower values of $\Gamma_D$ in BD simulations, the effective solvent viscosity was lowered to about $\eta^* \sim 0.01$, where $\eta^*$ is the solvent viscosity scaled by that of water. At these low values of solvent viscosity, BD simulations begin to exhibit inertial contributions in the
particle trajectories and the attachment rate of particles at the crystal surface is decreased relative to the diffusion coefficient. In the MD limit, the particle motion is purely inertial and this effect is maximized. Simply put, whether the attachment rate relative to bulk diffusion is reduced by inertial effects or by unsuccessful MMC moves does not affect the segregation behavior. In other words, the phenomenon of interfacial segregation during crystal growth is completely determined by the relative rates of particle diffusion to and attachment/detachment at the crystal surface, and the exact mechanism by which these rates are established has essentially no bearing on the final result. Because we are only interested in the relative rates of these two processes for understanding segregation, we are unconstrained by the criterion in eq. (2.32), keeping in mind that further increases in \( rd_{\text{max}} \) reduce the growth rate to impractically low levels.

In closing, we note an important limitation of running MMC simulations in this manner. The above conclusions are only valid because the physics of the problem are dominated by single particle processes. For example, in cases where cluster diffusion and coalescence are important, violation of eq. (2.32) in an MMC simulation would lead to incorrect results relative to those obtained from BD. Conversely, the agreement between the three simulation methods over a wide range of parameters confirms the single-particle nature of the overall process. Of course, one should keep in mind that the BD simulations employed here and in many literature studies themselves are limited in describing cluster diffusion. The omission of hydrodynamic interactions in BD simulations leads to incorrect scaling with cluster size for the center-of-mass diffusivity, as shown in eq. (2.33), which should be \( D_{\text{CM}}(n) \sim n^{-1/d} \) instead [61]. Including such
interactions dramatically increases the computational cost of direct simulation of crystal growth with the interaction models employed in this work.

Figure 2.16: The effect of $rd_{\text{max}}$ on single-component bulk fluid diffusivity and crystal growth computed with MMC simulations of 0.98\,\mu m diameter particles at a volume fraction of $\phi = 0.3$. (a) Self-diffusion coefficient in a bulk fluid phase, (b) Crystal growth rate, and (c) scaled growth rate, $\Gamma_D$. In all cases, $E_b = 3.75 \, k_B T$ (squares), $E_b = 4.25 \, k_B T$ (diamonds), and $E_b = 4.75 \, k_B T$ (circles). The dashed lines represent diffusion-limited conditions (see text).
2.6 Conclusion

A detailed computational study was performed of binary crystallization in a colloidal system. The inter-particle interactions employed in this work were specified by an analytical model that was validated by direct comparison to optical tweezer measurements, allowing for a quantitative comparison to experimental studies of binary crystallization. We find that the binary segregation behavior in the system can be described well by a simple model in which a hierarchy of interfacial processes, namely various types of particle detachments from the growth interface, competes with the overall growth rate of the crystal.

The observed segregation coefficient, interpreted through $N_{\text{eff}}$, was found to exhibit a stepped structure with respect to a dimensionless growth rate parameter, defined as the ratio of the crystal growth rate to the bulk fluid diffusivity. The stepped nature of the segregation behavior is a consequence of a separation between the rates of different particle detachment processes, which in turn results from the nature of the short-ranged DNA-mediated interactions (relative to the micron-scale spheres modeled here). Specifically, we find that surface particle detachment rates vary widely depending on the number of bonds formed with the crystal. The apparent segregation coefficient is then determined by the fastest detachment process that can still be equilibrated during crystal growth. For smaller particles, we find that the detachment rates become more closely spaced and the stepped nature of the apparent segregation coefficient gradually disappears, leading to the smoothly varying segregation behavior observed in atomic
systems where the energy landscape at the crystal surface is smoothed by the longer-ranged interactions.

A key aspect of our study is the use of non-equilibrium MMC simulations to accelerate crystal growth relative to diffusion and access a broader range of growth conditions beyond what is possible with standard Brownian dynamics simulations. In order to do this, the MMC simulations were performed with moves that were large relative to the interaction distance (but small relative to the colloid scale). These operating conditions were shown mathematically to lead to some artifacts, but ones that were not relevant for the phenomenon under investigation. Specifically, it was shown that collective dynamics, such as cluster diffusion, were erroneously arrested in our simulations, but that these types of processes were unimportant in the context of the segregation behavior. In other words, we find that, at least relative to BD simulations, cluster diffusion and coalescence are not significant avenues for crystallization. Obviously, colloidal interactions at higher volume fractions will become increasingly dependent on collective motions.
Chapter 3

Kinetic Control of Crystal Structure in DNA-Directed Self-Assembly

3.1 Introduction

The use of engineered DNA oligomers to direct the self-assembly of nano- and micro-scale particles into interesting ordered structures was first proposed almost fifteen years ago [2, 74], and realized only recently [11, 59, 79, 81, 112]. The underlying idea in this directed assembly approach is that single-stranded DNA oligomer brushes grafted onto spherical particles induce an interparticle attraction by the process of DNA hybridization. The utility of DNA-directed particle self-assembly stems from the possibility of specific adhesion or attraction. Mixed population of particles can be created such that only particle pairs bearing mutually complementary DNA strands will experience a reversible attraction due to the formation of transient DNA bridges [11]. In such a mixed sample, one can, in principle, engineer a matrix of different strength attractions amongst different sub-populations of particles by varying the amount and sequence of their respective bound DNA strands or the use of soluble DNA strands to mediate bridge formation [58].
Despite considerable theoretical attention [67, 101], the necessary conditions for DNA grafted particles to form high-quality, ordered arrangements remain incompletely understood [22, 93]. In particular, as the number of components within a given assembly grows, defect formation and kinetic limitations are expected to play increasingly significant roles. For example, we have recently demonstrated that kinetic limitations in the rates of particle attachment and detachment at the growth interface of compositionally disordered solid-solution binary colloidal crystals lead to unexpected segregation behavior and compositional distributions within the crystals [59, 93].

Here, we report a comprehensive computational analysis of the growth of ordered binary superlattice crystals, in which the interactions are governed by DNA bridging between particles. Our work is motivated by recent experiments [79, 81] that have realized ordered, binary crystalline assemblies of gold nanoparticles using DNA hybridization. In both of these studies, ordered superlattice structures were grown with the CsCl (body-centered cubic, or bcc) symmetry. These crystalline assemblies were formed by introducing two different types of single-stranded DNA oligomer brushes onto the nanoparticles, such that oligomer strands on “A” particles were partially complementary only to strands on “B” particles. For both particle sub-populations, like strands were designed to be non-hybridizing. Interestingly, one of the studies [81] also demonstrated, under certain experimental conditions in which the annealing rate was varied, the formation of a close-packed (cp) crystalline assembly, which was hypothesized to be a partially compositionally disordered, binary face-centered cubic (fcc) crystallite. These results provide the first indications that kinetic effects may play
important roles in setting the quality and even the very structure of crystalline assemblies formed by DNA-mediated interactions.

In this chapter we consider the crystallization of a binary system, Fig 3.1 a, having two sub-populations of same-sized spherical particles, “A” and “B”, with independently adjustable specific attraction strengths parameterized by $E_{AA}$, $E_{BB}$, and $E_{AB} = E_{BA}$. We use a pair-potential model for DNA-directed interactions that was developed by Biancianello et al. [11], and which has been verified quantitatively by direct measurements [58, 59]. Our results, however, should be generally applicable to any system with short-ranged attractions.

Major features of the expected phase behavior are summarized in Fig. 3.1 b. When all three pair attractions are similar in strength, (Fig. 3.1 b.i), a randomly substituted close-packed (cp) crystal is favored, due to its high coordination and density [31]. Increasing $E_{AA}$ relative to $E_{AB}$ and $E_{BB}$ leads to segregation of the B species (Fig. 3.1 b.ii), as reported in an earlier study [59]. Here, cp A-rich crystals are formed with a minority concentration of B particles that is determined by the relative strengths of the binding energies, $E_{AA}$ and $E_{AB}$, and the growth kinetics. Finally, the case $E_{AB} > E_{AA}, E_{BB}$, which is the primary focus of the present chapter, obviously favors mixing as shown in Fig. 3.1 b.iii. In principle, both bcc and cp-based superlattices should be feasible, and as noted above some evidence for their formation has already been generated in the literature [79, 81].
Figure 3.1: DNA-mediated assembly of binary systems with same-sized particles.  

- **a.i** – A and B spheres of the same size are distinguished by different grafted single-stranded DNA; 
- **a.ii** – linker DNA strands create dynamic bridges between particles; 
- **b.i** – equal interactions between all particles, $E_{AA} \sim E_{BB} \sim E_{AB}$, leads to random cp crystals with the system stoichiometry;  
- **b.ii** – the case $E_{AB} < E_{AA}, E_{BB}$ leads to demixed cp crystals with substitutional minority concentrations determined by interaction strengths and growth kinetics;  
- In both b.i. and b.ii., the bcc phase is expected to be unfavorable relative to cp;  
- **b.iii** – for $E_{AB} > E_{AA}, E_{BB}$, ordered superlattice structures are expected. Both cp and bcc superlattices are possible.
The remainder of the chapter is structured as follows. In Section 3.2, the possible 1:1 superlattice structures are identified in both the cp and bcc crystal systems, and order parameters are introduced to describe their ordering extent. In Section 3.3, we summarize the details of a perturbation theory framework for estimating the free energies of the various binary crystal and fluid phases. In Section 3.4, extensive Monte Carlo simulations are described for the growth of binary superlattice crystals as a function of various conditions. In Section 3.5, a thermodynamic-kinetic model is presented that describes mechanistically how the extent of ordering and crystal structure is set in the systems of interest. Finally conclusions are presented in Section 3.6.

### 3.2 Binary Superlattice Optimization

Possible superlattices comprised of an equal number of A and B particles were identified using lattice Monte Carlo optimizations (simulated annealing). Rigid, periodic fcc, hcp, rhcp, and bcc lattices were generated and lattice sites were randomly assigned with equal numbers of A or B designations. 500 lattice sites were employed for the cp (fcc, hcp, rhcp) lattices, while 432 sites were used for the bcc case. Monte Carlo moves consisted of selecting two particles at random and switching their identities, with the standard Metropolis criterion used to accept and reject moves [3]. The energy change corresponding to each move attempt was calculated based on the difference between bond energies on nearest neighbors, defined as $\Delta_{AB} = E_{AB} - E_{AA, BB}$. Over the course of the simulated annealing optimization, $\Delta_{AB}$ was increased gradually from $1.0 k_B T$ to $5.0 k_B T$. 

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by increments of $0.25k_B T$ every 1000 sweeps, where 1 sweep is defined as 1 move attempt per particle. By the time $\Delta_{AB} \sim 5.0k_B T$, the simulated annealing algorithm is effectively reduced to a local energy minimization. Each optimization was repeated several times to ensure that the global energy minimum was located in each case.

An order parameter was defined by counting the total number of unlike (A-B) bonds between nearest-neighbors and dividing by twice the number of particles in the system to account for the double counting of bonds. The resulting quantity is henceforth denoted as $N_{AB}$. In completely random systems with A:B stoichiometry of 1:1, $N_{AB}$ is 3 for cp crystals and 2 in bcc crystals; these values provide lower bounds on the order parameter, $N_{AB}$.

We find that all crystal lattices studied resulted in a maximum $N_{AB}$ value of 4; i.e. each particle was connected to 8 unlike first-nearest neighbors; examples of the ordered superlattices that corresponded to this $N_{AB}$ value are shown in Fig. 3.2 for the various lattices. The 8-fold coordinated bcc crystal leads to the expected CsCl superlattice (Fig. 3.2 a), in which each particle is surrounded by 8 unlike particles. The optimal value of the order parameter, $N_{AB}$, in the case of the 12-fold coordinated cp crystals is also exactly 4, although the superlattice structures appear to be somewhat different between the fcc, hcp, and rhcp cases; Figs. 3.2 b – d. In all of the cp cases, each particle is surrounded by 8 unlike nearest-neighbors and 4 like ones.
Corresponding unit cells for each type of superlattice are shown in Fig. 3.3. The fcc superlattice is of the CuAu type [13, 45], which possesses both face-centered cubic and face-centered tetragonal (fct) unit cells. Note that the tetragonal cell is comprised of two stacked cubic cells [13, 45]. Both types of CuAu unit cells are present in the Monte Carlo optimized fcc configuration shown in Fig. 3.2 c. It is notable that the order parameter, $N_{AB}$, is not influenced by switching from one unit cell to another within the binary fcc system. This flexibility extends to the hcp lattice, to interfaces between the hcp and fcc lattices, and therefore to the rhcp system. In Appendix C, a systematic approach is presented for analyzing the superlattice flexibility in each crystal system. Other superlattices, such as those based on the simple cubic (sc) lattice, are not favorable due to their large lattice free energy relative to the cp and bcc lattices. Note that the maximum value of $N_{AB}$ for sc is 3 because each particle has a maximum of 6 unlike nearest-neighbors.
Figure 3.2: Monte Carlo-based simulated annealing optimization of 1:1 binary systems on rigid lattices. \( a \) – bcc (CsCl); \( b \) – fcc (CuAu); \( c \) – hcp; \( d \) – rhcp. All superlattices exhibit \( N_{\text{AB}} = 4 \) ordering. For the class of short-ranged potentials considered in this thesis, all cp superlattices are energetically degenerate.
Figure 3.3: Unit cells for the various 1:1 superlattice structures obtained with on-lattice Monte Carlo optimization.  

**a** – Body-centered cubic (bcc-CsCl);  
**b** – Face-centered cubic (fcc-CuAu);  
**c** – Face-centered tetragonal (fct-CuAu);  
**d** – Hexagonal close-packed (hcp).

### 3.3 Thermodynamic Analysis of Ideal 1:1 Binary Superlattice Crystals

The Metropolis Monte Carlo (MMC) optimization results presented in the previous section suggest that both cp and bcc superlattice crystals are theoretically possible in the DNA-mediated interaction system, which is dominated by first-nearest neighbor interactions. We begin our analysis by computing free energies for the various possible phases in this system: cp superlattices, bcc superlattices, and fluid. All free energy calculations were performed using perturbation theory; details of the approach are
provided in Appendix D. Note that the free energy difference between the various cp lattices is zero within the perturbation theory employed here. In the remainder of this chapter, therefore, we do not make explicit distinction between the various cp phases, although the fcc lattice was used to represent the cp free energy calculations.

The minimum free energy of a given crystalline phase can be determined on the basis of either an open or closed system. In an open system, each phase can attain its minimum free energy independently, while in a closed system, the free energies are determined by computing a constrained coexistence condition between the fluid and crystal phases. Here, we show that for the short-ranged interaction potentials under consideration, the contribution of the fluid phase free energy is small at equilibrium, and therefore comparisons between the free energies for the different lattices can be made independently of the fluid phase.

To compute the equilibrium free energy within a closed system (constant number of particles, $N$, and volume, $V$), we apply the standard double-tangent method [103]. In this approach, the density of the coexisting phases is determined by first computing the free energies of the fluid and crystal phases as a function of density and then equating the pressures, $P$, and chemical potentials, $\mu$, for each phase to find the constrained free energy of each phase, where

$$\frac{P}{\rho k_B T} = \rho \left( \frac{\partial F / N k_B T}{\partial \rho} \right),$$

(3.1)
An example calculation for 300 nm spheres is shown in Fig. 3.4. In Fig. 3.4 a, free energies are computed as a function of reduced density, \( \rho = 6\phi/\pi \), where \( \phi \) is the volume fraction, for the equicomposition binary fluid, and perfect CsCl and CuAu superlattice phases. The following interaction potential parameters were employed: \( E_{AB} = 5k_B T \), \( E_{AA} = 0 \), and \( E_{BB} = 0 \). For these parameters, the CsCl superlattice is more favorable than the CuAu one, assuming that each phase is allowed to find its optimal volume fraction. The double tangent method was then used to compute the constrained equilibrium condition between the CsCl and fluid phases; we find that for the present example, the equilibrium volume fractions are \( \phi = 0.595 \) for the CsCl superlattice and \( \phi \sim 0.0013 \) for the fluid. The equilibrium volume fraction for the unconstrained CsCl superlattice is \( \phi = 0.60 \), demonstrating the weak effect of the fluid.

The perturbation theory results were compared to those from a direct NVT-MMC simulation with the same inter-particle potential and particle diameter. The simulation was initialized using a procedure introduced in chapter 2, which is designed to circumvent the large crystallization barriers present in short-ranged interaction systems. A periodic cubic simulation cell containing 5,000 randomly distributed, non-overlapping particles [51, 53] at a prescribed volume fraction, \( \phi = 0.3 \), is first allowed to relax to
constant energy at the prescribed temperature and volume. In this example, and all subsequent simulations described in this chapter, the binary system composition was 1:1. The presence of a large nucleation barrier leads to the formation of a metastable fluid phase [32]. Once the fluid is equilibrated, a spherical CsCl crystallite containing 150 particles is inserted into the center of the equilibrated fluid (replacing an equal number of fluid particles). The system is then allowed to further relax while keeping the seed particles fixed. When the surrounding fluid has equilibrated with the fixed seed, the seed particles are released and the entire system is allowed to further evolve without constraints. The criterion for seed equilibration is based on the number of “solid-like” particles identified in the seed; once this number reaches the initial seed size, the seed is deemed to be equilibrated. Solid particles are identified using a local bond order analysis [7, 96, 98], which is defined in chapter 2.

A snapshot of an equilibrated configuration for the parameters described above is shown in Fig. 3.4 b. The bcc crystal possesses a volume fraction of $\phi = 0.589$ and is in equilibrium with a fluid phase with volume fraction of $\phi \sim 0.04$, the latter containing 8% of the total number of particles. Note that the bond-order analysis used to identify solid particles generally underestimates the number of solid-like particles at the crystal surface, and therefore tends to overestimate the fluid volume fraction; much larger simulations would be required to eliminate this error. Nevertheless, the volume fractions obtained from the direct MC simulations are in good agreement with the results of perturbation theory. In general, for the simulations discussed later in this chapter, where $E_{AB} \geq 2k_B T$ and $\phi \geq 0.2$, the equilibrated solid crystallites (either bcc or cp superlattices) were
generally found to coexist with a dilute fluid phase with volume fraction of approximately \( 0.01 \leq \phi \leq 0.04 \), and which contained about 3 – 8% of the total number of particles within the system.

![Phase equilibrium evaluated by perturbation theory (a) and NVT-MMC simulation (b).](image)

**Figure 3.4:** Phase equilibrium evaluated by perturbation theory (a) and NVT-MMC simulation (b). a – free energy for a fluid (squares), cp superlattice (diamonds), and bcc superlattice (circles) as a function of the reduced density, \( \rho = 6\phi / \pi \). b – equilibrium snapshot from an NVT-MMC simulation at \( \phi = 0.3 \) with ~ 92% of the system forming the bcc superlattice crystallite (green and blue spheres) and 8% of particles remaining in the fluid phase (grey spheres). Simulation conditions: \( \sigma = 300 \text{ nm}, \ E_{AB} = 5k_B T \), and \( E_{AA} = 0 \).

### 3.4 An Equilibrium Phase Diagram for Superlattice Formation

The preceding considerations suggest that a phase diagram for predicting superlattice structure can be constructed on the basis of perturbation theory, and that the preferred crystal phase can be determined on the basis of unconstrained free energies. However, in
the perturbation theory calculations used to generate Fig. 3.4 a, it was assumed that both the CuAu and CsCl superlattice structures were ideal; i.e. perfectly ordered \( N_{AB} = 4 \). The MMC simulation snapshot in Fig. 3.4 b suggests that, at least under the conditions used in this example, it is in fact possible to grow perfectly ordered CsCl crystals from a seeded configuration. However, in general, this may or may not be the case; we have previously shown that kinetic and thermodynamic limitations may be important during the growth of binary solid-solution crystals using DNA-mediated interactions [59, 93].

In this section, we develop an equilibrium picture for superlattice ordering and use it to construct a map for superlattice formation. The independent variables in our analysis are the attractive strengths of the two inter-particle potentials, between like and unlike microspheres, which we represent here by the maximum well-depths, \( E_{AA} = E_{BB} \) \((= E_{AA,BB})\) and \( E_{AB} \), respectively. An energetic driving force for superlattice ordering can then be defined in terms of the binding energy difference, i.e. \( \Delta_{AB} = E_{AB} - E_{AA,BB} \). In the following discussion, we employ the term *antisite* to denote a single compositional ordering defect in a binary superlattice. Because colloidal systems are generally not able to undergo significant bulk annealing, only surface antisite defects are important during colloidal crystallization.

The average formation energy of a surface antisite defect, \( E_{\text{anti}} \), was estimated for both bcc and cp superlattices. Using the seeded growth procedure described in Section 3.3, numerous cp and bcc superlattice crystals were grown using different combinations of binding energies and system volume fractions. Further details of these numerical
experiments are provided later in Section 3.5. Several simulation configurations were isolated that contain almost perfectly ordered \( N_{AB} > 3.95 \) superlattice crystals of both bcc and cp type (see example configuration in Fig. 3.4 b). All particles that (1) possess at least one solid neighbor and (2) are under-coordinated relative to the bulk crystal phase were tagged. For each of these particles, the antisite formation energy, \( E_{\text{anti}} \), was computed by switching the site identity and noting the energy difference. The antisite formation energy was computed as an average over all surface sites (and thus surface orientations, because the crystallites were generally spherical), and expressed in terms of the binding energy difference, \( \Delta_{AB} \), so that \( E_{\text{anti}} = \alpha \Delta_{AB} \). Over all superlattice crystals sampled it was found that the energetic cost of a bcc surface antisite, \( E_{\text{anti}}^{\text{bcc}} \sim 2 \Delta_{AB} \), was substantially larger than that of a cp surface antisite, \( E_{\text{anti}}^{\text{cp}} \sim \Delta_{AB} \). As a result, for a given \( \Delta_{AB} \), the cp superlattice thermodynamically supports a higher surface antisite concentration. Note that \( E_{\text{anti}}^{\text{cp}} \sim \Delta_{AB} \) irrespective of whether the crystallite is rhcp, hcp, or fcc.

A simple thermodynamic model for the expected degree of ordering in binary cp and bcc crystals can be derived as follows. Let the probability that a particle crystallizes on a correct site be given by \( P_{\text{site}} \) and on an incorrect (antisite) be \( P_{\text{anti}} \), such that \( P_{\text{site}} + P_{\text{anti}} = 1 \). At equilibrium, \( P_{\text{anti}} \) and \( P_{\text{site}} \) are related by the condition

\[
P_{\text{anti}} = P_{\text{site}} \exp(-E_{\text{anti}} / k_B T)
\]

and therefore
\[
P_{\text{site}} \equiv \frac{P_{\text{anti}}}{\exp(-E_{\text{anti}}/k_BT)} = \frac{\exp(E_{\text{anti}}/k_BT)}{1+\exp(E_{\text{anti}}/k_BT)},
\tag{3.3}
\]

Because \(E_{\text{anti}}\) can theoretically possess any positive value, \(P_{\text{site}}\) ranges between 0.5 \(\leq P_{\text{site}} \leq 1\).

The compositional order parameter, \(N_{AB}\), which ranges from 3 (random) to 4 (perfect superlattice) in \(\text{cp}\) crystals, and 2 (random) to 4 (perfect) in \(\text{bcc}\) crystals, can then be mapped linearly onto \(P_{\text{site}}\). Thus, under quasi-equilibrium growth conditions

\[
N_{AB}^{eq}(\text{cp}) \sim 2 + 2 \frac{\exp(\Delta_{AB}/k_BT)}{1+\exp(\Delta_{AB}/k_BT)},
\tag{3.4}
\]

and

\[
N_{AB}^{eq}(\text{bcc}) \sim 4 \frac{\exp(2\Delta_{AB}/k_BT)}{1+\exp(2\Delta_{AB}/k_BT)},
\tag{3.5}
\]

where \(E_{\text{anti}}^{\text{cp}} \sim \Delta_{AB}\) and \(E_{\text{anti}}^{\text{bcc}} \sim 2\Delta_{AB}\) were applied in eqs. (3.4) and (3.5), respectively. Equations (3.4) and (3.5) represent theoretical models for the order parameter, \(N_{AB}\), in \(\text{cp}\) and \(\text{bcc}\) crystals grown under quasi-equilibrium conditions. Note that for both superlattice structures, the order parameter is entirely dependent on the binding energy difference between like and unlike pairs of particles.
The results in eqs. (3.4) and (3.5) are used as inputs to the perturbation theory described in Appendix D. For a given pair of inter-particle interaction strengths, $E_{AA, BB}$ and $E_{AB}$, the equilibrium ordering extent can be computed for both types of superlattices and then used to determine the corresponding free energies. The resulting phase diagram is summarized in Fig. 3.5 for particles with diameter, $\sigma = 300 \text{nm}$. The (green) diamonds delineate the bcc-fluid coexistence curve, (red) circles show the cp-fluid boundary, and the (orange) gradients show the bcc-cp boundary. The crystal-fluid coexistence lines were calculated based on a fluid phase with volume fraction, $\phi = 0.3$; these boundaries will shift upwards as the fluid volume fraction is reduced. The solid line labelled as “Random Solid Solution” represents a dividing line between ordered and phase-segregated cp crystals; the latter have been the subject of chapter 2 [59, 93] and are not considered further here.

The data in Fig. 3.5 indicates that for small enough $E_{AA, BB}$ the CsCl superlattice is favoured over the CuAu structure. The relative stability of the CsCl lattice arises from the fact that the cp lattice is higher in volume fraction, and for low $E_{AA, BB}$, the additional like-bonds in the cp superlattice actually increase the free energy of the system. Physically, this repulsion arises from an entropic penalty due to overlap between the non-hybridizing DNA brushes on adjacent like particles. As the value of $E_{AA, BB}$ increases, the additional enthalpic binding in the higher-coordinated cp structures shifts the balance in favour of cp superlattice crystals. Also shown in Fig. 3.5 are contour lines that show the value of the order parameter expected for different combinations of binding energy in the
cp portion of the phase diagram. For the parameter space considered here, the CsCl superlattice is almost perfectly ordered, i.e. $N_{AB}^{eq} \approx 4$ (contours not shown), while the cp superlattice requires a high antisite energy (which is proportional to the binding energy differential, $\Delta_{AB}$) to eliminate ordering defects.

**Figure 3.5:** Phase diagram for binary crystals grown under quasi-equilibrium conditions; Orange gradients – bcc-cp superlattice coexistence, green diamonds – bcc-fluid coexistence red circles – cp-fluid coexistence, dashed line delineates ordered superlattice crystals from phase separated or solid-solution crystals. Contour lines in the solid regions show the equilibrium value of the order parameter, $N_{AB}^{eq}$, for both superlattice types. Volume fraction, $\phi = 0.3$ and particle diameter, $\sigma = 300 \text{nm}$. 


3.5 Kinetic Limitations in Superlattice Formation

As noted in the previous section, the coexistence line between bcc and cp superlattices shown in Fig. 3.5 assumes quasi-equilibrium (i.e. slow) growth conditions, during which each growing crystal would be able to attain the equilibrium level of surface antisite defects. Using the MMC initialization procedure described in Section 3.3, a large number of seeded crystal growth simulations were performed in which the binding energies, the overall system volume fraction, and the particle diameter were varied. Overall parameters in the ranges, $\phi = 0.2 - 0.4$, $\sigma = 100 \text{nm} - 980 \text{nm}$, $E_{AB} = 3.0 k_B T - 7.0 k_B T$, and $\Delta_{AB} = 0.5 k_B T - 7.0 k_B T$ were considered. In some cases, the simulations were repeated using seeds in both the cp and bcc superlattice configuration. At the end of each simulation, the structure of the final crystal was determined using the radial distribution function and order parameter calculated. In order to eliminate the effect of introducing a perfect superlattice seed, only particles that were added to the seed during the subsequent growth were included in the calculation of the final order parameter.

Motivated by the form of eqs. (3.4) and (3.5), the compositional order parameter, $N_{AB}$, was plotted as a function of the binding energy difference, $\Delta_{AB}$, for all MMC simulation conditions; see Fig. 3.6. Also shown in Fig. 3.6 (solid and dashed lines) are the equilibrium order parameter isotherms as a function of $\Delta_{AB}$. Across the entire range of $\Delta_{AB}$ considered, the equilibrium ordering isotherms provide clear upper bounds on the
MMC-derived values of $N_{AB}$ for both the bcc and cp superlattices. It is notable that all MMC conditions that led to the growth of CsCl resulted in essentially perfectly ordered crystals (solid symbols), while the vast majority of cp cases exhibited significant compositional disorder in the resulting crystals. Qualitatively, differences between the ordering extent observed in direct MMC simulation and the quasi-equilibrium value would indicate the presence of kinetic limitations. In other words, the results in Fig. 3.6 seem to indicate that not only are cp superlattice crystals subject to higher equilibrium concentrations of ordering defects, but that they are also subject to additional defect formation due to kinetic limitations during growth.

![Figure 3.6](image)

**Figure 3.6:** Kinetic limitations for the seeded growth of binary bcc and cp superlattice crystals. The theoretical predictions for equilibrium compositional order are outlined by the dashed line for the bcc crystal and solid line for the cp crystal. The filled symbols represent the MMC simulated compositional order parameter for bcc crystals, while the open symbols are for cp crystals. Simulation conditions: $\phi = 0.2 - 0.4$, $\sigma = 100 \text{ nm}$ (blue squares), $300 \text{ nm}$ (green diamonds) and $980 \text{ nm}$ (red circles).
The effect of the choice of initial seed superlattice is more difficult to interpret. We find that the initial seed size, and its initial ordering extent, does not significantly affect the order parameter of a grown crystal. Interestingly, far away from the bcc-cp coexistence line, seeds with the “incorrect” superlattice structure are observed to undergo a rapid diffusionless transformation into the correct superlattice structure before continuing to grow. The nature of this transformation will be discussed in a future publication. It is more difficult to determine whether the MMC simulations are consistent with the phase diagram in Fig. 3.5 for binding energy combinations near the coexistence line. In fact, we find empirically that the CsCl superlattice appears to be preferred in some cases for binding energy combinations that lie slightly to the right of the coexistence line in Fig. 3.5; i.e. in the region where cp crystals are expected. The reason for this anomaly was investigated by considering further the apparent kinetic limitations in the growth of cp superlattice crystals.

3.5.1 A Thermodynamic-Kinetic Model for Compositional Ordering During Superlattice Growth

A simple mechanistic model was developed in order to analyze quantitatively the effects of any kinetic limitations on the ordering extent in superlattice crystal growth. Binary crystal growth is initiated at the fluid-crystal interface and is driven by two basic processes: (1) fluid particles arriving at the crystal surface and (randomly) occupying a
site or antisite, and (2), particle exchange between sites and antisites by surface diffusion. Under equilibrium growth conditions, process (1) is expected to be much slower than process (2) and the system is able to attain the equilibrium ordering extent, i.e. \( N_{\text{eq}}^{\text{AB}} \sim N_{\text{eq}}^{\text{AB}} \). However, under faster growth conditions, i.e. when process (1) is rapid or at least comparable to process (2), the arriving particles do not have sufficient time for full surface annealing.

In order to establish a quantitative model for surface annealing kinetics, estimates are required for the rates of processes (1) and (2). The arrival timescale of particles is governed by short-range diffusion at the interface between the fluid and crystal, i.e. \( \tau_{\text{arr}} \equiv L^2 / D \), where \( D \) is the diffusivity within the interface. We assume that this diffusivity is equal to the bulk fluid diffusivity because of the lack of solvent effects within MMC simulations. \( L \) is a characteristic length that fluid particles must travel on average before colliding with the crystal surface. An estimate for \( L \) can be made by considering the mean particle separation in the fluid, which is related to the particle number density, \( \eta \), i.e.

\[
L \approx \lambda \eta^{-1/3},
\]

where \( \lambda \) is an adjustable model parameter. Diffusion limitations in the system generally lead to a reduced fluid density near the surface of the crystal which are accounted for here by the single empirical regression parameter, \( \lambda \).
Process (2) proceeds through the surface hopping of particles between sites (S) and antisites (AS). This reversible annealing process is described by

\[
\text{AS} \xleftrightarrow{k_f k_b} \text{S},
\]

(3.7)

where \(k_f\) is the site-to-antisite transition rate and \(k_b\) is the reverse process. Now assuming that the system is spatially homogeneous, the transient evolution of this process is given by two coupled differential equations for the fraction of sites (\(f_S\)) and antisites (\(f_{AS}\)), i.e.

\[
\frac{df_S}{dt} = -k_b f_S + k_f f_{AS},
\]

(3.8a)

and

\[
\frac{df_{AS}}{dt} = k_b f_S - k_f f_{AS}.
\]

(3.8b)

The general solution for the equation system (3.8) is given by [30]

\[
f_S = c_1 + c_2 \exp\left(-(k_f + k_b)t\right),
\]

(3.9 a)

and

\[
f_{AS} = c_3 + c_4 \exp\left(-(k_f + k_b)t\right).
\]

(3.9 b)
where \( f_S + f_{AB} = 1 \). These expressions represent the temporal evolution of the probability of a particle existing at a correct/incorrect site following its arrival at a random site. For the cp crystal case, the site and antisite fractions can be related to the compositional order parameter, \( N_{AB} \), by the following relations: \( N_{AB}(f_S = 1) = 4 \) and \( N_{AB}(f_S = 0) = 3 \). The remaining constants in eqs. (3.9) are determined by the conditions \( N_{AB}(t = 0) = 3 \) and \( N_{AB}(t \to \infty) = N_{AB}^{eq} \). With the preceding considerations, and assuming that surface equilibration proceeds in competition with particle arrival, a thermodynamic-kinetic model for the ordering extent, \( N_{AB} \), in cp crystals is given by

\[
N_{AB}^{M}(cp) = (3 - N_{AB}^{eq}) \exp(-k_{rel} \tau_{arr}) + N_{AB}^{eq},
\]

where \( k_{rel} = k_f + k_b \). The bcc case can be derived in exactly the same manner, except that the initial condition is now replaced by \( N_{AB}(t = 0) = 2 \), and \( N_{AB}(f_S = 0) = 2 \). The resulting model is

\[
N_{AB}^{M}(bcc) = (2 - N_{AB}^{eq}) \exp(-k_{rel} \tau_{arr}) + N_{AB}^{eq}.
\]
where $\Delta E$ is the collective energy of the bonds that must be broken in order to allow the particle to diffuse along the crystal surface. Based on an analysis of site and antisite configurations on the surface of a cp superlattice crystal, we find $\Delta E_{AS} \sim E_{AA}$ and $\Delta E_S \sim E_{AB}$; i.e. on average, for either transition direction, only one bond needs to be broken in order to allow a particle to diffuse freely across the crystal surface. The surface diffusion rate is therefore given by

$$k_{sd} = \frac{D}{0.6\sigma^2},$$  \hspace{1cm} (3.13)

where the quantity $0.6\sigma^2$ represents the square of the distance between adjacent crystallization sites on the cp crystal surface.

Although the preceding model for surface annealing on the cp surface neglects multi-particle interactions and any effects of surface topology (e.g. steps and ledges), it is able to capture quantitatively the order parameter observed in the MMC simulations across a very broad range of simulation conditions. Shown in Fig. 3.7 is a comparison of ordering extent measured from MMC simulations and calculated using eqs. (3.10) and (3.11), with $\lambda \sim 0.4$ demonstrating the best overall agreement (see eq. (3.6)). This value of $\lambda$ is consistent with the expectation that some level of fluid density depletion due to diffusion-limitation is expected at the crystal-fluid interface.
Figure 3.7: Thermodynamic-kinetic model for binary superlattice crystallization. Ordering extent, $N_{AB}$, in cp (open symbols) and bcc (solid symbols) crystals from MMC simulation ($N_{AB}^S$) and thermodynamic-kinetic model ($N_{AB}^M$). (red) circles – $\sigma = 980 \text{ nm}$, (green) diamonds – $\sigma = 300 \text{ nm}$, (blue) squares – $\sigma = 100 \text{ nm}$. Insets show example cp crystallite configurations grown in MMC simulations with different extents of ordering. Top: $\phi = 0.2$, $E_{AB} = 5.5 k_B T$, $\Delta_{AB} = 5.0 k_B T$, $\sigma = 300 \text{ nm}$; Bottom: $\phi = 0.3$, $E_{AB} = 4.75 k_B T$, $\Delta_{AB} = 0.5 k_B T$, $\sigma = 980 \text{ nm}$.

3.5.2 Pseudo-Phase Diagrams for Superlattice Stability in Binary DNA-Mediated Systems

The results in Figs. 3.6 and 3.7 have potentially significant implications on the growth of superlattice crystals, and in particular those with cp stacking. Most of the simulation growth conditions considered here lead to cp crystals with substantially more
compositional defects than expected under equilibrium conditions, while those with bcc symmetry are almost perfect. As a result, kinetic limitations for ordering in cp crystals may affect the phase diagram shown in Fig. 3.5. In order to study this possibility further, we introduce a pseudo-coexistence line between cp and bcc superlattice crystals, which is now a function of both kinetic and thermodynamic factors. Instead of comparing crystal free energies on the basis of equilibrium ordering, we use the data in Fig. 3.7 to compute the actual ordering possible under the given simulation conditions. The ordering extent is now a complex function of the growth conditions, including binding energies, overall volume fraction, interaction range, and particle size.

In Fig. 3.8, the phase diagram generated previously based on equilibrium arguments is augmented to include an “operational coexistence line”, denoted by the cyan squares, in which free energies are compared on the basis of the actually realizable order parameter for given operating conditions, rather than the equilibrium order parameter. In Fig. 3.8 a, a volume fraction of $\phi = 0.1$ was used to perform the crystal growth simulations, which corresponds to relatively slow growth conditions, allowing the cp crystals to order to levels that are close to equilibrium. As a result, the operational coexistence line is close to the equilibrium coexistence line (orange gradient symbols), across the entire binding energy ranges considered. The contour (dashed) lines in Fig. 3.8 show the values of the order parameter attainable in cp lattice growth; comparison with Fig. 3.5 clearly demonstrates that kinetic limitations reduce the ordering extent, even under slow growth conditions. Finally, note that the fluid-solid coexistence lines are now located at higher values of binding energy, as expected. We also note that the visible
separation between the equilibrium and operational coexistence lines at the fluid-solid boundary arises from finite errors in the thermodynamic-kinetic model. In actuality, we expect that both cp-bcc phase boundaries should converge to a single value at the fluid-solid boundary because the growth rate becomes infinitesimally slow there.

The effect of kinetic limitation is more profound when the volume fraction of the system is increased to \( \phi = 0.4 \), and the growth kinetics are much faster relative to the ordering rate at the growing crystal surface; see Fig. 3.8 b. The operational coexistence line now moves significantly to the right, away from the equilibrium line, and indicates that the bcc phase is stabilized relative to realizable cp crystals in the region between the two coexistence lines. This is because cp crystals are unable to order to a large extent under these conditions, while the bcc crystals are still essentially perfect. Evidence of the poor ordering extent expected in cp crystals is provided by the contour lines in Fig. 3.8 b which are at significantly lower values that their counterparts in Fig. 3.8 a.
Figure 3.8: Pseudo-phase diagram for binary superlattice formation for non-equilibrium growth conditions. Orange gradients – equilibrium bcc-cp superlattice coexistence, cyan squares – operational coexistence line; green diamonds – bcc-fluid coexistence red circles – cp-fluid coexistence. Contour lines in the cp region show the expected value of the order parameter, $N_{AB}(cp)$, with kinetic limitations included. a – Volume fraction, $\phi = 0.1$; b – volume fraction, $\phi = 0.4$. For both cases, particle diameter, $\sigma = 300nm$. Blue circles located at $E_{AB} = 6.0 \ k_B T$ and $E_{AA, BB} = 1.4 \ k_B T$ represent conditions for unseeded, homogeneous nucleation simulations (see text).
This interesting result suggests that under high driving force for growth, the bcc superlattice phase is metastable relative to the cp phase. It also suggests that different operating conditions should lead to the observation of different superlattices, a result that is qualitatively consistent with the experimental findings in ref. [81] where different quenching rates in a binary gold nanoparticle system with DNA-mediated interactions were found to lead to both CsCl and partially disordered cp superlattice crystals. Before we address the experiments further, we discuss additional simulations in which superlattice crystals were nucleated homogeneously from the fluid without seeding. These simulations were used to establish whether our findings extend to the process of nucleation and whether in fact it would be possible to realize different crystal phases simply by modifying the operating conditions.

As mentioned earlier in the chapter, homogeneous crystallization is subject to large free energy barriers that require high driving forces to overcome in small simulation systems and in short times. We employed two different simulations, which are denoted by blue circles in Figs. 4.8 a and 4.8 b. In both cases, the binding energies were $E_{AB} = 6.0 \, k_B T$ and $E_{AA, BB} = 1.4 \, k_B T$, while the overall volume fraction was $\phi = 0.1$ (Fig. 4.8 a) and 0.4 (Fig. 4.8 b). Both 5,000-particle simulations were initialized with an equal number of A and B particles. Snapshots from the unseeded MMC simulations are shown in Fig. 4.9. Indeed, the spontaneously grown crystals are found to exhibit the kinetically expected structure. In the slow-growing $\phi = 0.1$ simulation, the crystal nuclei are all
highly ordered cp crystals. Manual analysis of the nucleated particles provides an estimated $N_{AB} \approx 3.95$, which is in excellent agreement with the thermodynamic-kinetic model prediction shown by the contour lines in Fig. 4.8 a. When the volume fraction is increased to $\phi = 0.4$, all nuclei are formed as perfect CsCl crystals, unambiguously confirming our overall mechanistic picture for the phase behavior in this system. Once again, we find evidence of a diffusionless transformation between the CsCl and CuAu superlattices once the CsCl crystallites grow further; this phenomenon is probed in detail in a forthcoming publication.
Figure 3.9: Snapshots of unseeded MMC simulations showing homogeneously nucleated binary superlattice crystals. Both simulations are initialized with 5,000 particles in the fluid phase ($\sigma = 300 \text{nm}$) and with equal numbers of A and B assignments. Binding energies are $E_{AB} = 6.0 \ k_B T$ and $E_{AA,BB} = 1.4 \ k_B T$. a – $\phi = 0.1$, b – $\phi = 0.4$. 
3.5.3 A Hypothesis to Explain Some Recent Experimental Findings

We conclude this section by returning to the experimental findings in refs. [79, 81]. Although it is tempting to explain how both bcc and cp crystals were found in the experiments of Park et al. using the model described in the previous sections, we note that this is only possible if some finite A-A interactions were present. As shown in Fig. 3.5, for cases where only A-B interactions are present, only the CsCl superlattice is expected to form. One possible source for like particle interactions is van der Waals (vdW) attraction between all particles in the system.

The vdW interaction between induced dipoles is a non-specific interaction that arises from continuous electronic cloud fluctuations within each particle. This type of interaction is subject to partial retardation via screening by fluctuations within the solvent when the inter-particle separation is larger than $\sim 10$ nm [46]. An empirical approximation for the partially retarded vdW attraction is given by [94]

$$E_{vdW} = \frac{-A_H\sigma}{h} \left[ \frac{2.45}{120p_0} - \frac{2.17}{360p_0^2} + \frac{0.59}{840p_0^3} \right], \quad (3.14)$$

where $A_H$ is the Hamaker constant; for gold nanoparticles in water, $A_H \sim 4 \times 10^{-19}$ J [46]. $h$ is the minimum surface-to-surface distance and $p_0 = 2\pi h/\lambda$, where $\lambda \sim 100$ nm is the
intrinsic electronic wave length of gold atoms [94]. Therefore, $p_0$ represents the relative strength of the electronic oscillations between neighboring particles.

The accuracy of eq. (3.14) depends on the magnitude of $p_0$ and is about 5% for $1 < p_0 < \infty$, 15% for $0.5 \leq p_0 \leq 1$, and should not be used for $p_0 < 0.5$ [94]. The binary gold nanoparticles used in ref. [81] are estimated to have $p_0 \sim 1$. Inserting this estimate into eq. (3.14) results in a non-specific binding energy of about $E_{vdW} \sim 1.4 k_B T$. This exercise suggests that it is indeed possible for vdW interactions to be present, and that they may be strong enough to place the binary system in the regime where kinetic control of superlattice structure is feasible. Of course, the particle size and DNA oligomers employed in ref. [81] are quite different from the ones used to motivate the present study and further simulations would be required to draw more definite conclusions. We finally note that no cp crystals were found in ref. [79] under any conditions. Interestingly, applying eq. (3.14) to the gold nanoparticle system used in ref. [79], provides an estimate for the vdW attraction, $E_{vdW} < 0.5 k_B T$. 
3.6 Conclusion

In summary, our results demonstrate several interesting aspects of DNA-mediated assembly that may be relevant for future experiments. First, some phases, such as the cp superlattice in this case, may be thermodynamically favorable but kinetically difficult to grow with high quality. Very constrained growth conditions were required in our simulations in order to achieve a high degree of order in these crystals, consistent with the disordered cp crystals observed experimentally in ref. [81]. On the other hand, the bcc superlattice was found to be exceptionally robust; in fact, it was not possible to find feasible simulation conditions that led to defected CsCl. The ability of our simulations to explain recent experimental findings, as well as predict quantitatively the required conditions for growing perfect cp and bcc superlattices makes our approach useful for predicting practical operating conditions to access regions of interest in more complex phase diagrams. More speculatively, our results also suggest the possibility that kinetic selectivity may be purposefully engineered to favor otherwise difficult-to-access structures in more complex systems. These issues are certain to become increasingly relevant as the degree of complexity employed in DNA-mediated assembly increases, with the fabrication of practically useful structures in mind.
Chapter 4

Summary and Future Work

4.1 Summary

Within this work, our colloidal suspension is comprised of two sub-populations of “A” and “B” particles, at various compositions (A:B). The DNA-mediated interaction for the system is short-ranged with three types of interactions: $E_{AA}$ (binding between A-A particles), $E_{AB}$ and $E_{BB}$. A realistic model pair-potential for the DNA-mediated interaction (outlined in chapter 2 and verified by experiments [11]) is used directly in our computational framework to investigate the self-assembly of DNA-functionalized colloids.

Through our computational framework, as outlined in Fig. 4.1, we have demonstrated that a strict thermodynamic view of self-assembly can not describe all features required to construct binary crystals from an aqueous suspension. In chapter 2, through a detailed study of segregated growth, we identified that a fix number of surface bonds are a requisite for particles with short-ranged interactions to crystallize. While in chapter 3, we demonstrated that the assembly kinetics play a critical role in selecting the structure of the observed binary crystal from suspension.
Figure 4.1: Computational framework for studying colloidal self-assembly. Crystal nucleation and growth is investigated through Monte Carlo and Brownian dynamic simulations. Perturbation theory is used to calculate the free energy of bulk phases.

4.1.1 Segregated Growth of Binary Crystals from Solid-Solutions

We observed the segregated growth of tracer “B” particles within a binary solid-solution of DNA-colloids through experiments and simulations. Here, the interaction strength of the system is $E_{AA} > E_{AB} > E_{BB}$, where $E_{BB}$ is engineered such that B-rich crystals are not assembled. Within the A-rich crystals, we determined the segregation coefficient, $k_{seg}$, (a ratio of the concentration of B particles in the bulk crystal to fluid) and measured the
crystal growth. Both experiments and simulations note that $k_{\text{seg}}$ is independent of the initial A:B composition of the bulk fluid.

A direct measure of the interfacial dynamics during crystallization is obtained from $k_{\text{seg}}$. At the fluid-crystal interface, fluid particles dynamically break and form bonds with the crystal surface allowing for annealing. Particles finally adhere to the crystal after a fix number of surface bonds are established. This number of bonds is directly measured by $k_{\text{seg}}$. Both experiments and our computational framework reported that two surface bonds are required for crystallized particles to permanently attach to the crystal surface. Our simulations revealed that under slower annealing, within the fluid-crystal interface, three surface bonds are required for incorporation into the growing crystal. However, for longer-ranged atomistic systems [10, 48], surface particles can form multiple bonds with different crystallization sites all at once. Upon the breakage of one bond, the particle is funneled towards the remaining crystallization sites. This process leads to a continuous segregated growth until an equilibrium number of bonds are formed.

The interfacial segregation during growth is completely determined by: (1) particle diffusion to the crystal surface, and (2) particle attachment / detachment at the crystal surface. The exact interfacial, segregation mechanism has essentially no bearing on the final result. Both our MMC and BD simulations deviate from the diffusion-limited conditions, (1) ~ (2), by decreasing (2) relative to (1). Within MMC this is accomplished by an increased rejection rate; while in BD, increasing the effect of inertia.
decreases attachment / detachment at the crystal surface relative to particle diffusion. The above conclusions are only valid for process dominated by single particle motion.

4.1.2 Kinetic Control of Structure in Self-Assembled Binary Crystals

As with segregated growth, kinetic plays an important role in the assembly of binary crystals from a suspension of DNA-colloids with $E_{AB} > E_{AA,BB}$ at A:B = 1:1. For same-sized A and B particles, the system can only self-assemble into cp (fcc, hcp and rhcp) or bcc crystals. Here, the role of kinetics within this system is observed through the compositional order, $N_{AB}$, of the assembled crystal. $N_{AB}$ of the binary crystals is used to calculate their free energy (through perturbation theory) and phase diagram.

We proposed a simple theoretical model for $N_{AB}$ under thermodynamic conditions (i.e no kinetic limitations), $N_{AB}^{eq}$. The kinetic limitations of the assembled crystal is identified by the comparison of $N_{AB}^{eq}$ to the simulated compositional order, $N_{AB}^{S}$, of the system. Under all simulated conditions bcc crystals exhibited no kinetic limitations as $N_{AB}^{S} \sim N_{AB}^{eq}$. While for a majority of the simulated growth conditions cp crystals experience kinetic limitations. This propensity towards kinetically limited $N_{AB}^{S}$ for the cp crystal results from its low energetic penalty for crystallizing defects (particle
located on an incorrect site) on the crystal surface. We presented a thermodynamic-kinetic model of limited compositional growth for binary crystals, which is in excellent agreement with $N_{AB}^S$.

$N_{AB}$ obtained from the thermodynamic-kinetic model is used to determine the free energy and phase diagram for candidate binary crystals. The effect of kinetics upon $N_{AB}$ for the cp crystal changes the bcc-cp phase boundary. Here, for a given interaction strength and at slower assembly kinetics, the cp crystal becomes more stable, $N_{AB}(cp) \rightarrow N_{AB}^{eq}(cp)$, and in some cases is even more stable than the bcc crystal. Thus, through $N_{AB}$, kinetic controls the structure of the assembled binary crystal.

Recent experiments [81] have observed the assembly of both cp and bcc crystals. Here, two different routines were undertaken to obtain the same interaction of the system: (1), the abrupt on switching of the system’s interaction and (2), the gradual increase of the system’s interaction until its final value is reached. For the first routine, the assembly kinetics is fast and bcc crystals are observed. While for the second routine, the assembly kinetics is slow enough that cp crystals assembled out of suspension, instead of the bcc crystals. Both the experimental findings and our simulations results establish that kinetics control the structure of the assembled crystal.

The computational results of this thesis outline the significance of kinetics on the self-assembly of binary crystals. As the complexity of colloidal systems increases, the
role of kinetics on self-assembly may be used as a route to access unfavorable thermodynamic crystalline structures.

### 4.2 Future Work

Thus far, within this dissertation, we have developed an efficient computational framework to investigate self-assembly of colloidal suspensions with DNA-mediated interactions. Due to the attractive features of the system, the computational studies performed in our work are readily compared to experimental data generated by our collaborators in the Crocker group. We have developed several computational tools to study nucleation and crystal growth for simple systems. Future work will be aimed at three major tasks:

1. **Assembly of more complex crystal structures.** Analyzing systems with additional degrees-of-freedom in order to determine whether it is possible to use DNA-mediated interactions to create more complex crystal structures. Examples include multicomponent systems in which both the particle sizes and interaction strengths are modified. We will consider the effects on nucleation and crystal growth of heterogeneous distribution of DNA spaces on the colloid surface.

2. **Expansion of computational framework.** Developing additional computational tools mainly based on Monte Carlo and Brownian dynamics to enhance sampling efficiency, particularly for computing nucleation barriers. The short-ranged interactions lead to sampling problems in the system phase space and several approaches including umbrella sampling, EXEDOS, and parallel tempering will be implemented and modified for our needs.

3. **Designing realistic DNA-mediated interactions for assembly of a targeted crystal structure.** Inverse modeling to find interaction potentials that would lead to interesting crystal structures. The inverse modeling would be constrained by
realistic bounds on what can be constructed using the DNA hybridization framework.

The following sections briefly discuss some of the possible directions that will be pursued.

4.2.1 Self-Assembly of Multicomponent System

The phase diagram for a hard-sphere system can be expanded by introducing an additional degree-of-freedom, such as colloidal size polydispersity (Fig. 4.2). The system’s free energy arises purely from entropy – the assembly of the maximum close-packed superlattice \([20, 44]\). With the addition of a very-short ranged attractive interaction, the colloidal superlattice structure will not vary appreciably (only a slight decrease of its volume fraction); now each colloid centered at its superlattice site will oscillate around the minimum of the interaction potential. It is vital that the potential allows for annealing of the colloids, i.e. the potential well-depth must be shallow enough to allow colloids to enter and leave via thermal fluctuations; without this mechanism crystallization into any superlattice structure is impossible.

The DNA-mediated colloidal system developed by the Crocker group has the advantage of being short-ranged and allows for annealing of the assembled colloids via thermal fluctuations. At a specific size ratio, we can investigate the effect of the DNA-mediated interaction on the stability of the LS, (L-large and S-small colloids) superlattice.
These investigations can serve as the basis for developing a fundamental theory for short-ranged interacting systems, which may be summarized as Fig. 4.2.

**Figure 4.2:** The close-packing density, $\phi(cp)$, as a function of the size ratio $\alpha (=S/L)$ for the CsCl, LS$_2$, LS$_3$, LS$_{13}$, and LS ~NaCl or NiAs structures. a, the packing limit of the fcc or hcp crystal of monodisperse spheres is shown by the horizontal line at $\phi(cp) = 0.7405$. The lower chart summarizes the regions of stability predicted by computer simulation (gray) and cell calculations (black) [44]. b, the NaCl lattice. c, the LS$_3$ lattice [20]. d, the CsCl lattice.

Increasing the colloidal size polydispersity further enriches the hard-sphere phase diagram of Fig. 4.2. The first step within this investigation of a multicomponent system is to identify superlattices that maximize the close-packing for a given $L_iS_jS_k$ combination. Once the stable superlattice for a given $L_iS_jS_k$ combination is known, the effect of DNA-mediated interaction upon this superlattice can be studied. Finally, we can
apply our methodology for the observation crystallization kinetics for DNA-mediated superlattices (of the form LS\textsubscript{j} or L\textsubscript{i}S\textsubscript{j}S\textsubscript{k}).

### 4.2.2 Heterogeneous Distribution of Interactions

The fabrication conditions of DNA-colloids can lead to heterogeneous distribution of spacers on the surface of the colloid. As schematically shown in Fig. 4.3 a, some particles within the system may have a denser distribution of surface spacers, which results in the formation of more DNA-hybridized bridges between these particles (and higher binding energy) compare to the overall system. The binding energy of the system, $E_b$, is based on the average surface coverage of DNA-spacers per particle, as outlined in chapter 2, and has a standard deviation of stdv. Here, the stronger binding particles will first nucleate within the system, due to their lower nucleation barrier. The binding of these particles are less conducive to annealing and growth from neighboring nuclei of different orientations leads to the formation of aggregates.

The effect of heterogeneity of the DNA-mediated interaction plays a major role in nucleation and crystal growth. As shown in Fig. 4.3 b, NVT-MMC (canonical) simulations of the homogeneous system, stdv = 0, do not experience spontaneous nucleation after $5 \times 10^9$ sweeps (1 MC move per particle). As the interaction heterogeneity is increased, more spontaneous nucleation events and formation of aggregates are
observed. Finally, we can determine the minimal stdv for a given $E_b$ that is required to allow annealing of nucleated particles to form crystals.

Figure 4.3: The effect of interaction heterogeneity on nucleation and crystal growth. **a.i**, homogeneous distribution with standard deviation (stdv) of 0.0. **a.ii**, example of heterogeneous distribution. **b**, NVT-MMC simulation of heterogeneous interactions (as measured by stdv). Simulation conditions: $\sigma = 0.98 \mu m$ and $\phi = 0.3$. 
4.2.3 Calculation of Nucleation Barriers

4.2.3.1 Non-Boltzmann Sampling

Non-Boltzmann sampling is often used to overcome the problem of sampling rare events, such as nucleation. This is accomplished by limiting the search of phase space ($\Gamma$) to relevant areas for the observation of rare events. The probability density for the non-Boltzmann sampled ensemble is

$$\rho_w(x^N) = \rho(x^N)W(x^N), \quad (4.1)$$

where $x^N$ is the coordinates of $N$ particles within the system, $\rho(x^N)$ is the configurational density of phase space, and $W(x^N)$ is a non-Boltzmann weight. Umbrella sampling and the so-called expanded ensemble density of states (EXEDOS) [19, 95, 113] are examples of non-Boltzmann sampling methods, which are discussed briefly below.

4.2.3.2 Umbrella Sampling

In the umbrella sampling method, inaccessible regions of $\Gamma$ (which are often associated with rare events) are rescaled to allow easier access. Now, a MC trajectory (a sequence of successive moves) with $H(x^N)$ is adjusted by a non-Boltzmann term or bias potential, $\omega(x^N)$, such that the Hamiltonian is defined as

$$H_w(x^N) = H(x^N) + \omega(x^N), \quad (4.2)$$
where $\omega(x^N)$ is small for the interesting class of configurations and very large for all others. It is these values of $\omega(x^N)$ that biases the MC trajectory towards sampling the class of rare configurations. To further increase the efficiency of sampling rare configurations important to $\omega(x^N)$ along some predefined reaction coordinate (defined here as a continuous pathway that connects two points within $I$ to each other), this method can be applied over a set of successive “windows”, where each window samples a portion of the reaction coordinate. Now, each window has its own weight ($W(x^N)$) for $\omega(x^N)$; as a result, any computed quantity such as the free energy of the system is known only to an arbitrary constant as shown in Fig. 4.4 a. Once the absolute free energy of any reference window is known, the remaining windows are adjusted to obtain a continuous free energy curve, as shown in Fig. 4.4 b.

**Figure 4.4:** A schematic of the umbrella sampling method.  
(a) the free energy within each window.  
(b) the adjusted free energy curve over all windows.
For umbrella sampling and all other non-Boltzmann sampling methods, the system’s trajectory within $\Gamma$ is governed by the typical MMC acceptance / rejection criterion modified by eq. (5.1), and is given as

$$acc(old \rightarrow new) = \min \left[ 1, \frac{\rho(new)W(new)}{\rho(old)W(old)} \right].$$

(4.3)

### 4.2.3.3 Expanded Ensemble Density of States (EXEDOS)

One disadvantage of umbrella sampling is that the weights $\{W(x^N)\}$ need to be known \textit{a priori}. This issue is resolved within the EXEDOS methodology [19, 95, 113] where $\{W(x^N)\}$ is calculated in a self-adjusting manner. The EXEDOS methodology is based on Wang and Landau’s original work [108] and explores the use of density-of-state (DOS) methods to calculate the free energy profiles in terms of a desired reaction coordinate or order parameter. EXEDOS has been used to study unfolding of proteins [87], crystallization [19], and arbitrary statistical properties of ensembles [71, 95, 113].

Nucleation barriers can be determined with EXEDOS if the reaction coordinate is selected to be the cluster size, $n$. Here, random walks along $n$ visit each state proportional to $W(n(x^N)) = 1 / g(n)$. The partition function, $\Omega$, of the expanded ensemble is given by

$$\Omega = \sum_{n=1}^{N} Z(n) g(n),$$

(4.4)
where $Z(n)$ is the partition function of the ensemble described by $\rho(x^N)$. During the course of the MMC simulations, the probability of visiting state $n$ is related to the partition functions by

$$P_n(x^N) = \frac{Z(n)g(n)}{\Omega}. \quad (4.5)$$

From expression (4.5), if all states of $n$ are visited equally then $g(n_i)/g(n_{i+1}) = Z(n_{i+1})/Z(n_i)$, and the physical meaning of $g(n)$ is apparent: the free energy difference between state $n_i$ and $n_{i+1}$ is the natural logarithm, ln, of their corresponding $g(n)$ – free energy is defined as $\ln Z(n)$.

The generalized Wang-Landau method [108] is used to determine $g(n)$ and is outlined as follows:

1. $g(n)$ for all $n$ is set to 1 and all histograms, $h(n)$, are set to zero.
2. The trial move is accepted according to eq. (5.3). After every trial move a histogram is updated, $h(n_i) \leftarrow h(n_i) + 1$, and $g(n_i)$ is modified by a constant $f > 1$ such that $g(n_i) \leftarrow g(n_i) f$ (initial value of $f$ is $e^1$).
3. Calculate the average $h(n)$, $<h(n)>$, if every value of $n$ is greater than $x$ % of $<h(n)>$ up $f_{j+1} = f_j^{1/2}$, set all $h(n)$ to zero. Return to step 2
4. Stop when $f_{\text{final}}$ is smaller than exp($10^{-8}$).

Non-boltzmann sampling techniques (implemented with a set of successive overlapping windows) are usually coupled with parallel tempering [39] to further increase the sampling efficiency of $\rho(x^N)$. Within parallel tempering, at regular intervals adjacent windows are allowed to communicate (and probabilistically swap
configurations). This communication increases the efficiency of sampling \( \rho(x^N) \) along the predefined reaction coordinate.

### 4.2.3.4 Umbrella-Sampling and Parallel Tempering

The hard-sphere system was used to develop and test a computational approach for computing nucleation barriers for a hard-core system. We implemented the Auer and Frenkel method [7], which divides the simulation into two parts: a NPT-MMC simulation of a pure fluid (zero cluster size) and an umbrella-sampled cluster in equilibrium with a surrounding fluid. In order to stabilize the umbrella-sampled cluster, the simulation trajectory in a given window is biased towards a cluster of size \( n_0 \), using a harmonic potential bias defined as

\[
\omega(r^N) = k_n(n(x^N) - n_0)^2, \tag{4.6}
\]

where \( k_n \) is the potential strength and \( n \) is the reaction coordinate. With this bias, the most frequently sampled cluster is \( n_0 \), and the frequency of sampling clusters of size \( n \) decreases as clusters are further away from \( n_0 \). With the aid of parallel tempering, the efficiency of sampling clusters on the periphery of the biased potential is increased by the swap and rearrangement of configurations between adjacent windows (each window has a different \( n_0 \)). Therefore, a single cluster can theoretically traverse the entire reaction coordinate. Segments of the evolution of clusters initially centered at \( n_0 = 20, 100 \) and 150 are shown in Fig. 4.5 a.
Continuous properties over the reaction coordinate, such as the free energy curve, are disjointed because each sampling window has a different biasing weight. As shown in Fig. 4.5b the Gibbs free energy curve versus \( n \) is not continuous such that \( \Delta G_i(n)/k_B T + b_i \), where \( i \) indicates a different window. For the unbiased fluid simulation, \( b_i \) is zero, and therefore, \( \Delta G(n) \) within this window is evaluated with respect to the isotropic fluid. The constant \( b_i \) (for each window) is determined by fitting the Gibbs free energy segments to a \( k^{th} \)-order polynomial, which is accomplished by a linear least-square fit. The resulting continuous \( \Delta G(n)/k_B T \) curve versus \( n \) is given in Figure 4.5c. We are able to clearly identify the (pre-, post-, and) critical cluster sizes. For a hard-sphere system at a reduced pressure, \( P\beta\sigma^3 \), of 16, our calculated nucleation barrier is in excellent agreement with the results of Auer et al. [7]. This verifies that that our implementation of the umbrella framework [7] is correct, as shown in Fig. 4.5.

We have found that the procedure outlined above is not able to sample the nucleation barrier in the DNA mediated system. The primary reason for this is that the short-ranged attraction leads to particles “sticking” together and makes the configuration sampling highly inefficient, which leads to ergodicity problems. Future work will be aimed at developing possible solutions for the calculation of the nucleation barrier in short-ranged interaction systems such as the DNA-mediated one considered here. One approach to overcome the sampling bias would be to replace the umbrella sampling technique with the EXEDOS framework.
**Figure 4.5:** Calculation of nucleation barrier for a hard-sphere system. **a,** parallel tempering between bias windows. **b,** the Gibbs free energy for each window centered at $n_0$. The green symbols are for the non-biased fluid simulation. **c,** nucleation barrier for a hard-sphere system at reduced pressure of 16. Our calculation of the hard sphere nucleation barrier (blue curve) compares well with Auer and Frenkel (red curve) [7]. **d,** a critical cluster of 130 particles. The solid and fluid particles are identified as green and red, respectively.

### 4.2.4 Inverse Design of Colloidal Interactions

There exist two design approaches to predict the colloidal interaction for the assembly of a target crystal: bottom-up [49] and top-down [88]. Traditionally, the bottom-up approach is the method of choice; one arrives at a desired crystal lattice by trial and error:
multiple design iterations (i.e. define a candidate potential then simulate and observe the crystal lattice then update the design potential). This approach can be extremely labor intensive. Moreover, the simulation of the designed potential might not even lead to crystallization because of fluid phase metastability. The top-down approach is based on optimization and is outlined as follows:

1. Define an objective function.
2. Generate candidate potential.
3. Optimize candidate potential.
   a. Compare the target crystal to stored crystals with a defined potential.
4. Test candidate potential.
   a. If constraints are not met, return to step 2.
   b. Store candidate potential with the minimal objective function, return to step 2.
   c. End simulation when all candidate potentials are tested.
5. Crystallize the target crystal via the metastable fluid by the chosen design potential.

**Figure 4.6:** Schematic for the Design of Candidate Potentials.
The objective function and constraints are defined before the implementation of Fig. 4.6. Rechtsman and co-workers [88] have defined two types of possible objective functions, the zero-temperature and near melting temperature, and simulation constraints, the target crystal must be energetically and mechanically stable. For the simulation constraints, the potential corresponding to the target crystal must ensure that the lattice is the ground-state (energetically favored) compare to the applied library of crystal lattices and all phonon frequencies are real.

It is our hope to use and extend the Rechtsman et al. [88] approach to design a DNA-mediated interaction that is experimental realizable and will assemble into the target lattice. The methodology will be tested and improved by developing other objective functions or constraints. This methodology will be applied to find optimal particle sizes for a given DNA spacer length.
Appendix A

Monte Carlo and Brownian Dynamics

Details

A.1 Monte Carlo (MC)

The classical expression for the partition function \( \Omega \) of \( N \) indistinguishable particles is given by

\[
\Omega = \frac{1}{N!h_{pl}^{Nd}} \int d\mathbf{x}^N d\mathbf{p}^N \exp \left[ -\left( H(\mathbf{x}^N,\mathbf{p}^N) / k_BT \right) \right], \tag{A.1}
\]

where \( h_{pl} \) is Planck’s constant, \( d \) is the dimension of the system, \( \mathbf{x}^N \) and \( \mathbf{p}^N \) are the coordinates and momenta for all particles within the system, respectively. The collection of \( \mathbf{x}^N \) and \( \mathbf{p}^N \) points constitutes a \( 2Nd \) dimensional phase space. The Hamiltonian, \( H(\mathbf{x}^N, \mathbf{p}^N) \), is the total energy of the system and consists of kinetic (\( K \)) and potential (\( U \)) energy terms, such that \( H = K(\mathbf{p}^N) + U(\mathbf{x}^N) \). Given that \( K(\mathbf{p}^N) \) is a quadratic function of the momenta, the integration over all momenta can be performed analytically. The configurational partition function, which depends only on the particle coordinates, is then
defined as  \( Z = \int d\mathbf{x}^N \exp\left[ -\beta U(\mathbf{x}^N) \right] \) where \( \beta = 1/k_B T \). The average of a quantity \( M(\mathbf{x}^N) \) is given by:

\[
\langle M \rangle = \frac{\int d\mathbf{x}^N \exp\left[ -\beta U(\mathbf{x}^N) \right] M(\mathbf{x}^N)}{Z}, \tag{A.2 a}
\]

\[
\langle M \rangle = \int d\mathbf{x}^N \rho(\mathbf{x}^N) M(\mathbf{x}^N), \tag{A.2 b}
\]

where \( \rho(\mathbf{x}^N) (> 0) \) is the configurational part of the total probability density, \( \rho(\mathbf{x}^N, \mathbf{p}^N) \).

The power of MC is evident when evaluating \( \langle M \rangle \) over all configurational space, \( \mathbf{x}^N \). To determine \( \langle M \rangle \) from expression (A.2) the immense configurational space has to be evaluated twice: once for calculating \( Z \) and then for \( \langle M \rangle \). This leads to computational inefficiency as all possible configurations will have to be calculated twice, or calculated once and store. MC circumvents this problem by visiting a representative number of configurations. Here, a transition between configurations is weighted by the Boltzmann of the Hamiltonian, \( \exp\left[ -\beta U(\mathbf{x}^N) \right] \), and the average value of \( M \) over a larger number of sampled configurations is equivalent to expression (A.2).
A1.1 Metropolis Monte Carlo (MMC)

In 1953, Metropolis and co-workers [72] introduced a MC method to calculate the equation-of-state of a liquid. At the heart of MMC is the assumption of microscopic (detailed) balance between an old state \((\text{old})\) and a new state \((\text{new})\). Here, the probability of moving from \(\text{old}\) to \(\text{new}\) is equal to the probability of moving from \(\text{new}\) to \(\text{old}\) so that

\[
\rho(\text{old}) \alpha(\text{old} \to \text{new}) \text{acc}(\text{old} \to \text{new}) = \rho(\text{new}) \alpha(\text{new} \to \text{old}) \text{acc}(\text{new} \to \text{old}), \quad (A.3)
\]

where \(\alpha\) is a stochastic matrix and \(\text{acc}\) is the acceptance probability for a proposed move. The stochastic matrix depends on the ‘recipe’ employed for proposing a move. If the proposed move is generated randomly without microscopic propensities, i.e. the proposed move is unbiased, then the stochastic matrix is symmetric and \(\alpha(\text{old} \to \text{new}) = \alpha(\text{new} \to \text{old})\). However, if the generated move is biased in any way then \(\alpha(\text{old} \to \text{new}) \neq \alpha(\text{new} \to \text{old})\). In the MMC method, the stochastic matrix is symmetric and is often referred to as the underlying matrix of the Markov chain. The acceptance / rejection criterion for sampling \(\rho (\mathbf{r}^N)\) is given by

\[
\text{acc}(\text{old} \to \text{new}) = \min \left[1, \frac{\rho(\text{new})}{\rho(\text{old})}\right], \quad (A.4)
\]

i.e., for \([\rho(\text{new}) / \rho(\text{old})] < 1\), the move from \(\text{old}\) to \(\text{new}\) is accepted if the probability density ratio is larger than a randomly generated number between \((0, 1)\).
The MMC algorithm naturally samples the constant NVT ensemble (canonical). In order to sample the constant NPT ensemble (isobaric and isothermal), both particle displacement and volume fluctuation moves are employed. If these moves are generated randomly, then the acceptance criterion for a trial move is given by

\[
\text{acc}(\text{old} \rightarrow \text{new}) = \min\left[1, \exp\left(-\beta \left[ (U(\text{new}) - U(\text{old})) + P\Delta V - \beta^{-1}N\Delta \ln V \right]\right)\right], \quad (A.5)
\]

where \(P\) is the applied external pressure, \(V\) is the volume of the system, \(\Delta V = V(\text{new}) - V(\text{old})\), and \(\Delta \ln V = \ln(V(\text{new})/V(\text{old}))\).

**A.2 Brownian Dynamics (BD)**

As with MMC, BD access different configurations of the colloidal suspension through a stochastic process described by Langevin equation (LE). Within LE, the transition from state \(\text{old}\) to \(\text{new}\) is determined by a force balance, where forces acting on particles in state \(\text{old}\) are drag, systematic and thermal. The implicit presence of solvent is included in LE through the thermal force. Here, the thermal force accounts for the bombardment of the solvent on the particles. LE approximates Brownian motion as the explicit solvent effects are not included. When particles move within the suspension, the transfer of their momentum to the surrounding particles is accomplished by the solvent resulting in a coupled particle-particle motion. This solvent effect is fully captured by SD through
considering all coupled particle-particle motion. However, for this work, the LE
description of Brownian motion will suffice and is given as

$$m_i \frac{dv_i(t)}{dt} = -m_i \gamma_i v_i + F_i + R_i,$$  

(A.6)

where $m_i$ is the mass, $\gamma_i$ is the friction coefficient and $v_i$ is the velocity of the $i^{th}$ particle.
The drag force due to the motion of the particle through the solvent is described as $-m_i \gamma_i v_i$.
The intermolecular and external interactions are included in LE through the systematic
force, $F_i = -\nabla_i U(x^i)$. The thermal force, $R_i(t)$, is Gaussian distributed and is not
correlated to $v_i$ or $F_i$. In other words, $R_i(t)$ is independent of prior velocities,

$$\langle v_i(t) R_i(t') \rangle = 0, \quad t' \geq t,$$  

(A.7)

and is independent of prior systematic forces,

$$\langle F_i(t) R_i(t') \rangle = 0, \quad t' \geq t.$$  

(A.8)

The probability distribution for the stochastic Gaussian force is given as

$$W(R_i) = \frac{1}{\left(2\pi \langle R_i^2 \rangle \right)^{1/2}} \exp\left(-\frac{R_i^2}{2\langle R_i^2 \rangle}\right),$$  

(A.9)

with zero mean $\langle R_i \rangle = 0$. Also, the stochastic force is time independent (stationary) and
shown by its autocorrelation function,
\[ \langle R_i(t)R_j(t') \rangle = 2k_B T m_i \gamma_i \delta \delta(t-t'), \tag{A.10} \]

where \( j \) is the \( j \)th colloid and \( \delta \) is the Dirac delta function. For the remainder of this text, the \( i \)-index for eq. (A.6) is omitted. Solutions to expression (A.6) are called Brownian dynamics (BD). van Gunsteren and Berendsen proposed an efficient approach for solving eq. (A.6) [36] by first integrating LE and then discretize the resulting solution. From their work, the transition between configurations is obtained by

\[
x(t_n + \Delta t) = x(t_n)[1 + \exp(-\gamma \Delta t)] - x(t_n - \Delta t)\exp(-\gamma \Delta t) \\
+ m^{-1} F(t_n)(\Delta t)^2(\gamma \Delta t)^{-2}[1 - \exp(-\gamma \Delta t)] \\
+ m^{-1} \dot{F}(t_n)(\Delta t)^3(\gamma \Delta t)^{-2}(0.5 \gamma \Delta t[1 + \exp(-\gamma \Delta t)]) \\
- [1 - \exp(-\gamma \Delta t)] + X_a(\Delta t) + \exp(-\gamma \Delta t)X_a(-\Delta t) \\
+ O[(\Delta t)^4]
\tag{A.11}
\]

where \( \Delta t \) is the time step of the integrator and the spatial change due to random collisions with the solvent is given as

\[
X_a(\Delta t) = (m\gamma)^{-1} \int_{t_n}^{t_n+\Delta t} [1 - \exp(-\gamma(t_n + \Delta t - t))] R(t) \ dt.
\]

It should be noted that \( X_a(\Delta t) \) is correlated with \( X_{a-1}(\Delta t) \) for the same time interval over \( R(t) \). As a result, \( X_a(\Delta t) \) and \( X_{a-1}(\Delta t) \) are sampled from a bivariate Gaussian distribution [80]. For BD simulations, it is assumed that the stochastic force, \( R(t) \), is constant over the \( \Delta t \) interval and the order of the correlation time for \( R(t) \) is \( \Delta t \). In order to generate the required Gaussian process for \( R(t) \), expression (A.11) is limited to the condition, \( \Delta t \ll \gamma^{-1} \), that is, the correlation
time of the stochastic force is much smaller than the velocity correlation (relaxation) time, \( \gamma^{-1} \).

As the friction within the system decreases, \( \gamma \to 0 \), the BD algorithm reduces to the molecular dynamics (MD) Verlet algorithm [3] without consideration of the solvent, where the solvent viscosity (\( \eta \)) is \( \eta \sim 0 \) [36]. In other words, \( \eta \) effectively transforms BD into MD simulations by its decrease to zero (i.e. both \( \gamma \) and \( F_{\text{rand}}(t) \) become negligible as \( \eta \) approaches zero). As with the MD Verlet algorithm, eq. (A.11) has no explicit velocity consideration, however the velocity expression is given as

\[
v(t_n) = \left\{ [x(t_n + \Delta t) - x(t_n - \Delta t_n)] + m^{-1} F(t_n)(\Delta t)^2 (\gamma \Delta t)^{-2} G(\gamma \Delta t) \right. \\
\left. - m^{-1} \hat{F}(t_n)(\Delta t)^3 (\gamma \Delta t)^{-3} G(\gamma \Delta t) \right.
\]

\( + [X_n(-\Delta t) - X_n(\Delta t)] \frac{H(\gamma \Delta t)}{\Delta t} \)  

(A.12 a)

where

\[
G(\gamma \Delta t) \equiv \exp(\gamma \Delta t) + 2\gamma \Delta t - \exp(-\gamma \Delta t),
\]

(A.12 b)

and

\[
H(\gamma \Delta t) \equiv \gamma \Delta t \left[ \exp(\gamma \Delta t) - \exp(-\gamma \Delta t) \right].
\]

(A.12 c)
Appendix B

Evaluation of the Fokker-Planck Drift and Diffusion Terms by Monte Carlo

The Fokker-Planck equation that describes the evolution of the probability, \( P(X,t) \), for a Brownian particle is given as

\[
\frac{\partial P(X,t)}{\partial t} \approx -\frac{\partial}{\partial X} \left[ A(X) P(X,t) \right] + \frac{1}{2} \frac{\partial^2}{\partial X^2} \left[ B(X) P(X,t) \right],
\]

(B.1)

where \( X \) is coordinate of the particle, \( A(X) = \frac{\langle \Delta X \rangle}{\Delta t} \) is averaged drift velocity and \( B(X) = \frac{\langle (\Delta X)^2 \rangle}{\Delta t} \) is the diffusion of the particle. Kikuchi and co-workers showed that MC can solve for \( \langle \Delta X \rangle \) and \( \langle (\Delta X)^2 \rangle \) during some “time” interval, \( \Delta t \), for the ball-and-spring model [56]. They accomplished this by expanding \( \langle \Delta X \rangle \) and \( \langle (\Delta X)^2 \rangle \) up to the square of the maximum displacement, \( (rd_{\text{max}})^2 \).
Before deriving our expansion of \( \langle \Delta X \rangle \) and \( \langle (\Delta X)^2 \rangle \), we note details of typical acceptance probabilities for moves within MC simulations. The change in potential energy is given as \( \Delta E = \frac{\partial E}{\partial X} \Delta X = \frac{\partial E}{\partial X} (r d_{\text{max}} \xi) \), where \( \xi \) is a random number with a range of -1 to 1. If \( \Delta E < 0 \), the move of the system is to a lower energy state and the move is accepted with probability of \( 1/Z \), where \( Z \) is the large finite number of new states. For \( \Delta E > 0 \), the probability that particles move to a new state is given by \((1/Z) \exp(-\Delta E/k_b T)\). Now if we assume that \( \partial E/\partial X < 0 \) (with no loss of generality), \( \langle \Delta X \rangle \) can be written as

\[
\langle \Delta X \rangle = \sum_{\Delta X > 0} \frac{1}{Z} \Delta X + \sum_{\Delta X < 0} \frac{1}{Z} \exp \left( -\frac{1}{k_b T} \frac{\partial E}{\partial X} \Delta X \right) \Delta X .
\]  

For simplifying the notation within the derivation of the expansion of \( \langle \Delta X \rangle \), we define

\[
\alpha \equiv \frac{1}{k_b T} \frac{\partial E}{\partial X} \Delta X = \frac{1}{k_b T} \frac{\partial E}{\partial X} (r d_{\text{max}} \xi) .
\]

For small \( \alpha \) (due to Brownian motion), the expansion of \( \langle \Delta X \rangle \) to its \((rd_{\text{max}})^3\) term is given as

\[
\langle \Delta X \rangle \approx \sum_{\Delta X > 0} \frac{1}{Z} \Delta X + \sum_{\Delta X < 0} \frac{1}{Z} \left( 1 - \alpha + \frac{\alpha^2}{2} \right) \Delta X + O(\Delta X)^4 ,
\]  

(B.4a)
\[ \approx \frac{1}{Z} \left( \sum_{\Delta X > 0} \Delta X + \sum_{\Delta X < 0} \Delta X \right) + \sum_{\Delta X < 0} \frac{1}{Z} \left( -\alpha + \frac{\alpha^2}{2} \right) \Delta X + O(\Delta X)^4, \quad (B.4b) \]

and for constant \( \frac{\partial E}{\partial X} \),

\[ \langle \Delta X \rangle \approx -\frac{1}{k_B T} \frac{\partial E}{\partial X} \left( \frac{rd_{\text{max}}}{\delta t} \right)^2 \sum_{\xi < 0} \frac{\xi^2}{Z} + \left( \frac{1}{k_B T} \frac{\partial E}{\partial X} \right)^2 \left( \frac{rd_{\text{max}}}{2 \delta t} \right)^3 \sum_{\xi < 0} \frac{\xi^3}{Z} + O(rd_{\text{max}})^4, \quad (B.5) \]

finally for small \( |\xi| \), the summation over \( \xi \) is equal to an integral over \( d\xi \),

\[ \langle \Delta X \rangle \approx -\frac{1}{k_B T} \frac{\partial E}{\partial X} \left( \frac{rd_{\text{max}}}{\delta t} \right)^2 \int_{\xi < 0} \xi^2 d\xi + \left( \frac{1}{k_B T} \frac{\partial E}{\partial X} \right)^2 \left( \frac{rd_{\text{max}}}{2 \delta t} \right)^3 \int_{\xi < 0} \xi^3 d\xi + O(rd_{\text{max}})^4, \quad (B.6) \]

where \( \int_{\xi < 0} \xi^n d\xi \) is half the interval of \( \int_{\xi} \xi^n d\xi \equiv \frac{1}{1} \int_{-1}^{1} \xi^n d\xi \). Now, the expansion of \( \langle \Delta X \rangle \)

reduces to

\[ \langle \Delta X \rangle \approx -\frac{1}{k_B T} \frac{\partial E}{\partial X} \left( \frac{rd_{\text{max}}}{\delta t} \right)^2 + \left( \frac{1}{k_B T} \frac{\partial E}{\partial X} \right)^2 \left( \frac{rd_{\text{max}}}{16} \right)^3 + O(rd_{\text{max}})^4. \quad (B.7) \]

With the definition of \( \alpha \), expression (B.3), \( \langle (\Delta X)^2 \rangle \) can be written as

\[ \langle (\Delta X)^2 \rangle \approx \sum_{\Delta X > 0} \frac{1}{Z} (\Delta X)^2 + \sum_{\Delta X < 0} \frac{1}{Z} \exp(-\alpha)(\Delta X)^2 + O(\Delta X)^4. \quad (B.8) \]
For small $\alpha$, the expansion of $\left\langle (\Delta X)^2 \right\rangle$ in terms of $(rd_{\text{max}})^3$ is given as

$$\left\langle (\Delta X)^2 \right\rangle \approx \sum_{\Delta X > 0} \frac{1}{Z} (\Delta X)^2 + \sum_{\Delta X < 0} \frac{1}{Z} (1-\alpha)(\Delta X)^2 + O(\Delta X)^4,$$  \hspace{1cm} (B.9a)

$$\left\langle (\Delta X)^2 \right\rangle \approx \left( \sum_{\Delta X > 0} \frac{1}{Z} (\Delta X)^2 + \sum_{\Delta X < 0} \frac{1}{Z} (\Delta X)^2 \right) - \sum_{\Delta X < 0} \frac{\alpha}{Z} (\Delta X)^2 + O(\Delta X)^4,$$  \hspace{1cm} (B.10b)

for constant $\frac{\partial E}{\partial X}$ and small $|\xi|$, 

$$\left\langle (\Delta X)^2 \right\rangle \approx \left( rd_{\text{max}} ight)^2 \int_{\xi} \xi^2 d\xi - \frac{1}{k_B T} \frac{\partial E}{\partial X} \left( rd_{\text{max}} \right)^3 \int_{\xi < 0} \xi^3 d\xi + O(rd_{\text{max}})^4.$$  \hspace{1cm} (B.11)

Finally, the expansion of $\left\langle (\Delta X)^2 \right\rangle$ is determined by solving the integrals of $\xi$ and is given as

$$\left\langle (\Delta X)^2 \right\rangle \approx \left( rd_{\text{max}} \right)^2 \frac{1}{3} \frac{\partial E}{k_B T \partial X} \left( rd_{\text{max}} \right)^3 + O(rd_{\text{max}})^4.$$  \hspace{1cm} (B.12)
Appendix C

Analysis of Superlattice Formation in CP Lattices

In this section, we outlined a detailed approach to analysis the extent of order for all cp superlattices. These cp superlattices have distinct domains of perfect order, \( N_{AB} = 4 \), as well as interfaces between domains of different orientations. Furthermore, particles along the interface occupy similar environments of perfect order resulting in no lost of symmetry, and the overall cp superlattice preserves its perfect order.

A detailed inspection of the superlattice interface identifies the important traits of the interface. For the fcc superlattice interface shown in Fig. C.1 a, all particles within rows along the [010] direction are of the same type, which we denote as \( \forall[010] \). Adjacent superlattice domains which line the interface have alternate stacking of A and B particles in the [101] and [100] directions. Another important trait of the superlattice interface is that the stacking of A and B particles is symmetric to both superlattice domains, which results in the zero interfacial energy. These traits of the superlattice interface for the \( \forall[010] \) primitive axis can be extrapolated to other primitive axes, namely the \( \forall[100] \) and \( \forall[001] \) directions.
Figure C.1: Superlattice interface graph (SIG) for the fcc lattice. The fcc superlattice (a) has all particles within the [010] direction of the same type, \( \forall [010] \). The superlattice domains are outlined in (a) forms the superlattice interface identified by SIG, (b).

The combination of all extrapolated traits results in a concise representation of all fcc superlattice interfaces and is shown in Fig. C.1 b as the superlattice interface graph (SIG). Here a node of SIG is a direction of order within a domain and the edge (double headed arrow) between nodes is the superlattice interface between domains. Note, that the only possible superlattice interfaces for a given \( \forall [...] \) within a lattice are located on the opposite half of SIG from \( \forall [...] \). If there exists no \( \forall [...] \) then that lattice is not an ordered superlattice.

The cubic unit cell representation of SIG is transform to a hexagonal cell representation through the conversion of the directional Miller indices to Miller-Bravais indices. Hexagonal symmetric crystals, such as hcp and rhex, do not have the same set of indices in equivalent crystallographic directions. This problem is circumvented by the
introduction of a four-axis, Miller-Bravais coordinate system, where three axes \((a_1, a_2\) and \(a_3)\) define the hexagonal base plane. The fourth, \(z\)-axis is perpendicular to the basal plane. The conversion factors to change the Miller indices to the Miller-Bravais are given as

\[
[xyz] \rightarrow [uvtw],
\]

\[
u = \frac{n}{3}(2x - y), \quad v = \frac{n}{3}(2y - x), \quad (C.1 \ a)
\]

\[
t = -(u + v), \quad w = nz, \quad (C.1 \ b)
\]

where \(n\) is a factor that may be required to reduce \(u, v, t,\) and \(w\) to the smallest integers and \(u \ a_1 + v \ a_2 = -t \ a_3.\)

SIG with the Miller-Bravais indices identifies all superlattice interfaces within the hcp and rhcp lattices. As shown in Fig. C.2, the superlattice interface for the hcp superlattice is identified within the hexagonal base plane. With \(\forall[0001],\) both superlattice interfaces identified by SIG (Fig. C.2 c) are present within the basal plane of Figs. C.2 a and b, which results in a saw-tooth pattern of alternating \(A\) to \(B\) rows. The adjacent hexagonal plane (small particles within Fig. C.2 b) also contains a similar saw-tooth patterning.
Figure C.2: Superlattice interface graph (SIG) for the hcp lattice. The hcp superlattice is comprised of alternating $I, J$ hexagonal planes (a); all small particles in (b) are within $J$ planes; within the [0001] direction, all particles are of the same type, $\forall[0001]$. c – SIG for hcp superlattice.

The power of SIG with Miller-Bravais indices is fully utilized in the rhcp lattice, where the superlattice interfaces now exist between different types of lattices. The rhcp lattice consists of the random arrangement of three hexagonal base planes ($I, J$, and $K$), with adjacent planes of opposite type, as shown in Fig. C.3 a. This random alignment of hexagonal base planes results in the rhcp lattice being comprised of the fcc and hcp
lattices. For the rhcp superlattice, each fcc and hcp lattices are superlattices with appropriate interfaces defined by SIG and stacking of particles within adjacent trivalent hollows. Each trivalent hollow consists of three particles arranged into an equilateral triangle, which form a hexagonal plane. Superlattice interfaces between different lattices are only possible if both lattices share a common interface for alignment of particles in their respective $\forall[...].$ As shown in Fig. C.3, the hcp superlattice with $\forall[0001]$ (Fig. C.3 c) and the fcc superlattice with $\forall[1\overline{2}1\overline{3}]$ (Fig. C.3 d) forms a rhcp superlattice interface with alternating $A$ and $B$ particles in the $[11\overline{2}0]$ direction.
Figure C.3: Rhcp superlattice interface between hcp and fcc domains. a – rhcp superlattice; b – superlattice interface graph (SIG) for the rhcp lattice; c – hcp superlattice domain within (a); d – fcc superlattice domain within (a). All particles within the [0001] direction for the hcp superlattice and [\bar{T}2\bar{T}3] direction for the fcc superlattice are of the same type.
Appendix D

Perturbation Theory for Free Energy Estimation

D.1 Single Component

Classical perturbation theory (PT) was used to compute free energies for both the fluid and crystal phases considered in this paper [8, 9, 38, 86, 117]. In this Appendix, we briefly summarize the salient features of PT and provide details regarding how it was extended to the binary systems in this work. In PT, the total free energy is decomposed into two contributions, one arising from a reference state and one from a perturbation away from the reference. At a given particle density, $\rho$, the total free energy, $F$, of a phase is given as

$$F(\rho) = F_\alpha(\rho) + \int_0^\infty g_\alpha(r) E_\alpha(r) r^2 dr , \quad \text{(D.1)}$$

where $F_\alpha$ is the free energy of the reference state, $g_\alpha(r)$ is the radial distribution function of the reference state at $\rho$, and $N$ is the number of particles. The 2$^{nd}$ term on the rhs of
eq. (D.1) is the free energy contribution associated with the perturbative potential, \( E_p \).\n
\( E_p \) is defined such that the actual intermolecular interaction, \( E \), is a sum of the reference potential and \( E_p \).

We employ a hard-sphere (HS) reference state, for which the fluid is described by the well known Carnahan-Starling equation-of-state [14]. An analytical expression for the hard-sphere radial distribution function, \( g_r(r) \), in the fluid phase is taken from refs. [15, 105]. For the crystal phase calculations, the reference free energy was obtained by considering hard-spheres placed on lattice sites corresponding to the particular crystal phase (e.g. fcc or bcc) and applying the accessible free volume-per-particle model [104]. The \( g_r(r) \) function for crystals was approximated by summing Gaussian density functions around each particle [86].

The DNA oligomer brushes on the particles considered in this work produce a soft repulsion that requires a reference state different than simple hard spheres and we employ the Weeks, Chandler and Andersen (WCA) theory [109] for this purpose. In WCA, the a potential is decomposed into a reference \((WCA,r)\) and perturbation \((WCA,p)\) so that

\[
E = E_{WCA,r} + E_{WCA,p},
\]

\[
E_{WCA,r} = \begin{cases} 
E + \varepsilon, & r < r_{\text{min}} \\
0, & r \geq r_{\text{min}} 
\end{cases},
\]

(D.2)
$$E_{WCA,p} = \begin{cases} -\varepsilon, & r < r_{\min} \\ E, & r \geq r_{\min} \end{cases},$$

where $\varepsilon$ is the maximum well-depth of $E$, and $r_{\min}$ is the location of the maximum well-depth in the full potential function. Equation (D.1) can be rewritten in terms of the WCA decomposition, i.e.

$$\frac{F[\rho]}{Nk_B T} = \frac{F_{WCA,r}[\rho]}{Nk_B T} + 2\pi \rho \int_0^\infty g_{WCA,r}(r) E_{WCA,p}(r) r^2 \, dr. \quad (D.3)$$

Weeks and co-workers determine $F_{WCA,r}$ and $g_{WCA,r}(r)$ by equating the free energy between the $WCA,r$ reference and an equivalent HS system of diameter $d_{HS}$ [109]. This is accomplished by first determining the rate-of-change of $F_r$ with respect to the Boltzmann of the reference free energy, $\psi = \exp(-E_r / k_B T)$, and is given as

$$\frac{\partial F_r}{\partial \psi} = -\frac{k_B T \rho^2}{2} y_r(r), \quad (D.4)$$

where $y_r(r) = \exp(E_r / k_B T) g_r(r)$ is a continuous function of the spatial correlation.

Now, as the reference state is varied from HS to $WCA,r$, $F_{WCA,r}$ is evaluated by a Taylor series expansion around the HS reference state, such that

$$\frac{F_{WCA,r}}{k_B T} = \frac{F_{d_{eq}}}{k_B T} - \frac{1}{2} \int \rho^2 y_r \Delta \psi \, dr + O\left((\Delta \psi)^2\right), \quad (D.5 \, a)$$
where $\Delta \psi \equiv \psi_{\text{WCA}, r} - \psi_{d_{\text{HS}}}$. $d_{\text{HS}}$ is determined by equating the second term on the rhs of equation (D.5) to zero, such that

$$
\int_{d_{\text{HS}}}^{\infty} y_r r^2 dr = \int_{0}^{\infty} y_r \exp(E_{\text{WCA}, r} / k_B T) r^2 dr . \quad (D.6)
$$

As a result of finding the appropriate $d_{\text{HS}}$, the WCA reference free energy and spatial correlation ($y_{\text{WCA}, r}$) are equal to a HS reference of diameter $d_{\text{HS}}$ such that $F_{\text{WCA}, r} \approx F_{d_{\text{HS}}}$ and $y_{\text{WCA}, r} \approx y_{d_{\text{HS}}}$. Note that the above expression is applicable to both the fluid and crystal phases.

### D.2 Extension to Binary Systems

In order to accommodate binary systems in which only a small end portion of the grafted DNA strands is different in the two constituents, we assume that the entropic repulsion arising from the DNA brush is the same for both species, and therefore a single reference state can be employed. Now, for the binary system with (same-sized) A and B particles, the intermolecular interaction is written as

$$
E(r) = E_r(r) + E_{p,\alpha\beta}(r_{\alpha\beta}) , \quad (D.7)
$$
where $\alpha$ and $\beta$ denote the particle type so that

\[
E_{p,\alpha\beta}(r_{\alpha\beta}) = \begin{cases}
E_{p,\alpha\alpha}(r) , & \alpha = \beta \\
E_{p,\alpha\beta}(r) , & \alpha \neq \beta.
\end{cases}
\]  

(D.8)

Note that all like-interactions are represented by the subscript ‘AA’ because $E_{AA} = E_{BB}$.

Combining expressions (D.3) – (D.8) gives

\[
\frac{F[\rho]}{k_b T} = \frac{F_{r}[\rho]}{k_b T} + 2\pi \rho \int_0^\infty \left( g_{AA}(r)E_{p,AA}(r) + g_{AB}(r)E_{p,AB}(r) \right) r^2 \, dr ,
\]  

(D.9)

where $g_{AA}(r)$ and $g_{AB}(r)$ are the partial radial distribution functions for similar and dissimilar particles, respectively.

For crystalline phase calculations, A and B particles are arranged on the appropriate lattice to produce a desired value of $N_{AB}$ in the given crystal configuration. The number of similar $(n_{i,AA})$ and dissimilar $(n_{i,AB})$ particles present within the $i$-th layer from the central particle is therefore known a priori. With this information, $g_{AA}(r)$ and $g_{AB}(r)$ are defined, as in the single-component case, by Gaussian density functions around each particle such that $g(r) = g_{AA}(r) + g_{AB}(r)$. Similar considerations apply for binary fluids. In this case, $g_{AA}(r)$ and $g_{AB}(r)$ can either be directly measured from simulations of equilibrated (homogeneous) fluids, or can be obtained analytically as in the single-component case by assuming that the particle identities in the system are
randomly assigned at the specified composition. Both approaches were found to produce essentially identical estimates for $g(r)$.

Comparison of eqs. (D.9) and (D.1) suggests that an effective interaction potential for the binary system should be defined as

$$E_{\text{eff}}(r) \approx g_{AA}(r)E_{AA}(r) + g_{AB}(r)E_{AB}(r) / g(r).$$  \hspace{1cm} (D.10)

Now, the WCA decomposition can be applied directly to the effective binary potential, so that

$$E_{\text{eff}} = E_{\text{eff, WCA}, r} + E_{\text{eff, WCA}, p},$$

$$E_{\text{eff, WCA}, r} = \begin{cases} E_{\text{eff}} + \varepsilon, & r < r_{\text{min}}, \\ 0, & r \geq r_{\text{min}}, \end{cases} \hspace{1cm} (D.11)$$

$$E_{\text{eff, WCA}, p} = \begin{cases} -\varepsilon, & r < r_{\text{min}}, \\ E_{\text{eff}}, & r \geq r_{\text{min}}, \end{cases}$$

and the same procedure for evaluating the reference free energy and radial distribution function as that used for the single component case can be applied. That is, for the binary system, the free energy is given as

$$\frac{F[\rho]}{Nk_B T} = \frac{F_{\text{eff, WCA}, r}[\rho]}{Nk_B T} + 2\pi\rho \int_0^\infty g_{\text{eff, WCA}, r}(r)E_{\text{eff, WCA}, p}(r)r^2 \, dr,$$ \hspace{1cm} (D.12)
and the evaluate HS reference system with diameter $d_{HS}$ is determined through eq. (D.6). After determining $d_{HS}$, $F_{\text{eff,WCA},r} \approx F_{d_{HS}}$, evaluated through expression (D.12), and $\exp(E_{\text{eff,WCA},r} / k_BT)g_{\text{eff,WCA},r}(r) \approx \exp(E_{d_{HS}} / k_BT)g_{d_{HS}}(r)$ are readily calculated.

The approach presented in eqs. (D.7) – (D.12) was tested for a binary fluid with $E_{AB} = 5k_BT$, $E_{AA} = 2k_BT$, and $\sigma = 980 \text{ nm}$. Here, the assumption of a single reference state for all inter-particle interactions was relaxed within direct MMC simulations of the binary fluid, i.e. similar and dissimilar inter-particle interactions have different reference states. As shown in Fig. D.1, the radial distribution function for the reference state of the binary fluid, $g_{\text{eff,WCA},r}(r)$, obtained using eq. (D.12) and from direct MMC simulations are in excellent agreement. As a result, the above approach is valid for binary systems with short-ranged inter-particle interactions.
Figure D.1: Radial distribution function for a binary fluid. The analytically determined RDF is evaluated via perturbation theory (solid line), while the numerical RDF is obtained using binary MMC simulations with 5000 particles (circles). Simulation conditions: $E_{AB} = 5 k_B T$, $E_{AA, BB} = 2 k_B T$, $\sigma = 980 \text{ nm}$, A:B=1:1 and $\phi = 0.3$. 

\[ r/\sigma \] 

\[ g_{g_{w,Cf}}(r) \]


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