Ordered nanostructures through colloidal self assembly

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Ordered Nanostructures through Colloidal Self Assembly

by

Koh Yaw Koon

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2007

Signature of author: _____

Koh Yaw Koon
AMM&NS Program

Certified by: _____

Assoc. Prof. Wong Chee Cheong
SMA Fellow, NTU
Thesis Advisor

Certified by: _____

Prof. Yet-Ming Chiang
SMA Fellow, MIT
Thesis advisor

Accepted by: _____

Prof. Choi Wee Kiong
Program Co-Chair
AMM&NS Program

Accepted by: _____

Prof. Carl Thompson
Program Co-Chair
AMM&NS Program

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ABSTRACT

The fabrication of ordered nanostructures plays an important role in the realization of the potential of nanotechnology and consequently, it has become an intense field of research in recent years. One promising method of fabrication is the self assembly process of colloidal particles into ordered structures. The process is highly efficient but suffers from the drawback that defective structures form under most experimental conditions. This is due to the lack of understanding of the underlying mechanism. In this thesis, the process is investigated in order to help in the understanding. This is achieved by monitoring the structural changes *in-situ* during the process. The method of monitoring makes use of a property of the nanostructure known as the photonic bandgap. The bandgap is strongly dependent on the quality of the structure and can be monitored easily by simple optical methods. One important result of the experiments is the identification of a transition structure during the self assembly process. The driving force for the transition structure is the microscopic interaction forces between the particles in suspension. This observation highlights the inadequacies of previous studies where the driving force for colloidal self assembly is solely attributed to capillary forces. By combining both the interaction and capillary forces, the mechanism of self assembly is elucidated. With the new understanding, the origin of defects can be identified. Finally, conditions for growth of high quality nanostructures by colloidal self assembly are also identified.

Keywords: self assembly, colloidal crystal, photonic bandgap, *in-situ* monitoring, ordered nanostructure

Thesis Advisors:

1. Assoc. Prof. Wong Chee Cheong, SMA Fellow, NTU
2. Prof. Yet-Ming Chiang, SMA Fellow, MIT

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Chapter 1: Introduction

The ability to control matter on the scale smaller than 1 micron has opened up the minds of new generation of scientists about the potential of nanotechnology. The conceptual origin of nanotechnology can be traced back Richard Feynman at an American Physical Society meeting in 1959 where he gave a talk named “There’s Plenty of Room at the Bottom”. At the talk, Feynman described a process by which the ability to manipulate individual atoms and molecules might be developed, using one set of precise tools to build and operate another proportionally smaller set, so on down to the needed scale. In the course of this, he noted, scaling issues would arise from the changing magnitude of various physical phenomena: gravity would become less important, surface tension and Van der Waals’ attraction would become more important.

When materials shrink to the nm regime, interesting physical properties can arise. For example, when semiconductor crystals are shrunk to 1-10 nm, the energy levels can no longer be approximated as a continuous band [1]. The energy band is replaced by discrete energy levels, at which point the material can be classified as a quantum dot. The amazing property of quantum dots is that the spacing between the levels can be tuned by varying the size of the crystals. The luminescence property will be affected and the quantum dots can florescence at different wavelength of light. At nm scale, quantum effects become significant and effects that have been ignored previously reappear to produce extraordinary properties. There are many other examples of interesting phenomena that appear when matter is scaled down to nm scale like nanowires and nanotubes.

It gets even more interesting when structures with periodicity in the nm range are realized. Drawing inspiration from solid state physics, periodic structures have been found to exhibit interesting and useful properties attributable to structure. In solid state physics, the underlying periodicity in the atomic lattice can interact strongly with the electron wave-function. This is possible as the electron wave-function is of the same length scale as the lattice. One of the most important consequences of this interaction between the atomic lattice and the electron wave is the appearance of an energy bandgap. This gives rise to semiconductor materials which is one of the most important material classes in practical use. In addition to electron waves, there are other particle-waves that are known in nature. Thus, it can be expected that when structures with the right periodicity interact with particle waves with a commensurate length scale, interesting phenomena will occur. One important particle-wave is photonic or electromagnetic waves. When dielectric structures are fabricated with periodicity in the length scale of the wavelength of light, they inherit a new electronic structure known as a photonic bandgap. More discussion on photonic bandgap is done in Chapter 3 of this report. Other particle-waves like phonons [2], plasmons [3] can also show bandgap behavior when materials are structured periodically. Another interesting phenomenon is the concept of negative refraction in nano-structured materials [4, 5].

A common theme throughout the discussion so far is the ability by researchers to create structures on the order of nm scale. The methods to fabricate such structures can be categorized into two categories, top-down and bottom-up methods. In “top-down” methods, bulk materials are machined down to the required dimensions and periodicity. This usually involves some form of lithography to produce patterns and subsequent

material removal by various etching methods. This method of fabricating features of nm size has been extremely successful. It forms the backbone of modern microelectronics processing with multi-billion wafer fabrication facilities being built to perform the process. The advent of the electronics age can be traced to this ability to produce features in nm length scale over large areas. There is no doubt that this method of fabrication will continue to be improved to achieve better results. A difficulty in this method is to produce large 3D nanostructures. Most of the patterns that are produced by lithography are 2D in nature so for them to be extended to 3D, stacking of 2D structures has been proposed. An example of stacking is shown in Fig. 1.1. Also, research in areas like holographic lithography has produced encouraging results. However, these typically require much more advanced optical system to create 3D structures. Another difficulty lies in the resolution of etching. Some extreme examples of nanostructures require atomic resolution. However, the stochastic nature of etching makes it extremely difficult to achieve such resolution.

Fig. 1.1 Stacking of 2D patterned layers to form 3D nanostructures. (Sandia National Lab)

The second method of fabricating nanostructures is by “bottom-up” methods. The most representative method in this category is the self assembly process. Self assembly is a highly effective route to fabricate well-defined, 3D structures (Fig. 1.2). In this process, building blocks like molecules or mesoscale objects can be designed to spontaneously organize themselves into relatively stable long-ranged ordered structures. The key to the process is that the final structure is close to or at a thermodynamic equilibrium state. Ideally, the formation of defects is suppressed in the self assembly process as this constitutes a deviation from the equilibrium state. The final structure is determined by the selection of the building block which can be defined by characteristics such as topology, shape and surface functionality. Inherently, the self assembly process is highly parallel, making this approach well-suited for large-scale production where low cost and high throughput are important requirements.

Fig. 1.2 Example of self-assembled nanostructure. Nano-particles order spontaneously to produce a close-packed structure

Nature has been making use of self assembly to produce structures in the nm scale. For example, the wings of certain species of butterflies show brilliant iridescence when

viewed at an angle [6]. This is due to the presence of a self-assembled nanostructure on the wings (Fig. 1.3). Another example is the natural gemstone, opal. These colorful gemstones are made up of nm scale silica particles arranged in an ordered structure as shown in Fig. 1.4. Such knowledge has motivated researchers to seek methods of self assembly to produce highly ordered 3D nanostructures.

Fig. 1.3 Optical image of the butterfly wing showing brilliant iridescence and SEM images to show the nanostructure that produces the observed colors. [6]

Fig. 1.4 Natural opal with its brilliant colors and SEM image of the underlying structure that gives rise to the optical properties.

Several self assembly methods to fabricate the 3D PBG materials include phase separation of block co-polymer [7, 8] and crystallization of colloidal particles. In this thesis, the process of self assembly of colloidal particles will be examined. Colloids are dual-state materials containing a finely dispersed material in one state suspended in a continuous medium of another state. In this case, the colloidal system is that of solid particles in a liquid medium. The size of the particles can range from 10 μm to a few nm. These particles can be of any material class. Solvents in which the particles are suspended include most solvents with water being one of the most common suspension medium. Due to the inhomogeneous nature of colloids suspension, they can exhibit various interesting properties, which will be discussed in detail in Chapter 2 of this report. Various important industrial compounds are colloidal in nature. Examples include paints and polishing slurry. Also, colloids play an important role in powder processing where many precursors consist of particles suspended in solvents. The recent proposal to make use of the colloidal suspension to form 3D nanostructures has initiated a flurry of activities to investigate their properties.

Besides application as 3D photonic bandgap materials, self assembled colloidal nanostructure (or colloidal crystals) can also be used in other applications like catalysis and sensors. One drawback of the colloidal self assembly method is the difficulty to obtain extremely large area colloidal crystal with low defect density. This problem is due to the poor understanding of the self assembly process. The purpose of this report is to address this lapse in knowledge. To our knowledge, there has not been any in-depth study to understand the colloidal self assembly process. Initial demonstration of the process attributed the origin of ordering to capillary forces acting between the particles at the liquid-vapor interface [9]. However, this idea works

extremely well only for 2D particle arrays because capillary forces are related to surfaces and thus, 2D in nature. The capillary forces can not be incorporated easily into the 3D growth of colloidal crystals. Additional forces must be identified to provide the driving force for 3D self assembly. The microscopic interaction forces between the colloidal particles provide the needed driving force. This thesis addresses the gap in understanding the combined effect of multiple driving forces acting on self assembling system of uniform colloidal particles. In many ways, the 3D self assembly process is like the crystal growth process. The latter has been intensely studied and is well understood, resulting in large perfect crystalline silicon ingots being routinely grown for the microelectronics industry. In the case of colloidal crystals, they can grow in the same way as the normal crystals but the resulting structure is mechanically weak and easily affected by the capillary forces. It is hoped that this report will offer the first glimpse of the self assembly process and possibly results in the ability to grow highly ordered 3D nanostructures for practical applications. The defining idea of this report is the possibility of making use of the photonic bandgap properties to identify the colloidal crystal structural changes. This allows us to look at the self assembly process as it occurs through time without the need to resort to highly sophisticated methods. The results of the experiments tally well with theoretical consideration, thereby reinforcing the soundness of our model.

A brief summary of the various sections in this report will be shown as follows. As will be explained in detail in Chapter 2, particles in suspension interact with one another. The nature of colloidal suspension means that they have an extremely high surface to volume ratio. This also means the interactions within the suspension are intimately related to the surfaces. This can be seen from the review of the theory in

colloidal interactions. The interaction forces provide the driving force for crystallization in colloidal systems, which are also discussed in this section. In the final section of the chapter, a review of the synthesis of colloids will be presented. The discussion on the various aspects of colloid science is to help the reader understand some of the observed results in our experiments. However, the short discussion is not enough to cover the entire field of colloid science as it is vast and multi-disciplinary. Interested reader can look up some of the references that are cited throughout the report for more in-depth discussion of colloidal systems.

Chapter 3 reviews the concept of photonic bandgap. The fundamentals of the existence of a photonic bandgap in a periodic structure will be presented. This photonic property is important when we make use of the idea of the intimate relationship between the bandgap and the structure to track the self assembly process. This is an important point of the report as this is the direct experimental validation of the model of the self assembly process. Mainly, two ways of predicting the position of the bandgap will be shown in this chapter so that it can be used later on to extract information about the structures.

In chapter 4, the first attempt to examine the structural changes is reported. This is first done in a sessile drop configuration. Firstly, the reason for choosing the configuration is explained based on the conditions at the edge of the sessile drop. Then, the results of the in-situ photonic bandgap measurements will be presented to explain the changes in the structure. From the results, an intermediate transition structure is identified which plays a pivotal role in the self assembly process. The transformation from the transition structure to the final structure is attributed to be the origin of cracks

observed in colloidal crystals. The last part of the chapter is focused on some observation about the cracking process.

After looking at the structural changes, it is natural to extend the idea to other configuration of self assembly. In chapter 5, vertical deposition geometry is used to validate the model and highlight the universality of the model. Similar experiments are conducted with modifications to accommodate for different geometries. Similar changes in the structure can be extracted from the results. By the end of this chapter, the model for colloidal self assembly (divided into various stages) will be clarified.

A more detailed explanation of the role of the macroscopic boundary will be presented in chapter 6. Usually, the 3D nanostructures grown by the colloidal method need to be extracted from the solvent prior to use. This means that the colloidal crystal has to go through the highly disruptive process of drying which may destroy any equilibrium structures in solution. The stresses in this case arise due to the presence of the two macroscopic boundaries of the substrate and the meniscus. Based on the characteristics of the boundaries, the interactions between the boundaries and the particles will be examined. Possible outcome of the effect on the self assembly process will be presented with some simple experimental results.

Finally, the strategies to minimize the defect density in self assembled colloidal crystals will be discussed in chapter 7. Experimental results showing the possibility of these strategies will also be presented. The idea in this chapter will be useful for future attempts to grow highly ordered 3D nanostructures by colloidal self assembly. After this chapter, a conclusion of the report will be given and some suggestions for future work in the area will be presented.

Chapter 2: Colloids

2.1 Interactions in colloidal systems

Colloidal systems can crystallize at high concentrations and goes through processes like phase transition, nucleation and growth roughly analogous to the transformations seen in atomic systems [10-12]. The length scale of colloids is much larger than that of atoms and so the time scale of colloidal processes is several orders of magnitude slower than that of the atomic process. These characteristics make colloidal systems more accessible experimentally. For example, micron-sized particles can be easily observed under an optical microscope. The time for a 1 μm particle to reach its terminal velocity in water is around 1 microsecond which means that processes like phase transitions can be easily monitored by using high speed digital video microscopy [13]. There is tremendous effort in the scientific community to study the interaction forces between colloidal particles, in hope that it is possible to control the interactions and study their effects on important processes [14]. In this way, important insights about the atomic systems can also be obtained. In the following section, a description of the theoretical understanding in colloidal interactions will be presented.

An important theory of colloidal interaction was developed in the 1940s and its name bears the initial of the main contributors to the theory, namely Derjaguin, Landau, Verwey and Overbeek (DLVO) [15-18]. It was developed to describe the forces between charged surfaces interacting through a liquid medium and can also be used to describe the charged colloidal interaction forces after some modifications. The essence of the DLVO theory is that the interaction forces between colloidal particles is the sum

of repulsive electrostatic and attractive Van der Waals' forces. With the DLVO theory, a quantitative understanding can be developed to explain some of the early experimental observations about colloidal systems. Now, both the theory for electrostatic and Van der Waals' forces will be discussed and finally combined to look at some of the characteristics of the DLVO potential.

2.2 Electrostatic Interaction

Firstly, in order to understand the theory for electrostatic interaction in colloidal suspension, the physical properties of the system has to be explained. The colloids used in experiments are normally charge-stabilized colloids, meaning that they possess a surface charge. The surface charge provides the repulsive force that is necessary to stabilizing the suspension against agglomeration. In this case, mono-disperse colloid suspension is used as the model system for DLVO theory. The uniformity in the charges and size means that the colloids will always sense another identical particle, ensuring that the electrostatic force will always be repulsive. This can be thought as the simplest system in colloidal interactions and can be thought as an elemental noble gas system.

For a charged surface in a polar solvent like water, it will be surrounded by an atmosphere of different ions from the solvent. These co-ions or counter-ions could have similar or opposite polarity of electrostatic charge as the surface charge, depending on surface functionalization. The counter-ions produce a screening effect on the electrostatic force and limit the range of interactions beyond the surfaces whereas the co-ions can be thought as non-actors in the interactions. Thus, an important condition to establish is the distribution of the counter-ions in the solvent

in the presence of a charged surface. The simplest model for the counter-ions distribution is by Helmholtz [19] in which the ions are modeled as a fixed layer of charge positioned adjacent to the surface. However, this model is overly simplified. In a more refined model by Gouy and Chapman [17, 18, 20], the counter-ions form a diffuse double layer (Fig. 2.1) adjacent to the surface and are distributed according to a balance between their thermal motion and forces of electrical attraction. At this point, it is useful to discuss about the origin of ions in the solvent. A possible origin of ions in a polar solvent is the dissociation of the solvent molecules themselves. This will make the analysis much more complicated as the presence of the charged surfaces can affect the chemical equilibrium but it is adequate to approximate the ionic concentration as the bulk concentration at some distance away. Another origin of ions is added ions. The concentrations of these ions are normally fixed which means that they are easier to control. In pure water, the pH is 7 which mean that there are 10^{-7} M of H^+ and OH^- ions. In practice, ionic strength typically exceeds 10^{-4} M and the concentration of dissociated solvent ions can be ignored.

Fig. 2.1 The diffuse electric double layer around a charged surface in a polar solvent.

The potential of the region adjacent to the surface can be quantified by combining the Poisson equation for the electrical potential as a function of charge density with the Boltzmann equation for the counter-ions distribution due to thermal effects. The assumption here is that the surface charges are continuous and uniform. Also, the discrete nature of the solvent molecules is ignored, being integrated in an effective field, making this a mean field theory. There is general agreement that the DLVO theory is valid for most cases, the remaining criticism being in the validity of some of the assumptions. The Poisson-Boltzmann (PB) equation that describes the potential due to such a charge distribution looks like this:

$$\varepsilon_o \varepsilon_r \nabla^2 \Phi = -e \sum_i z_i c_{io}^* \exp(-z_i e \Phi / kT) \quad (1)$$

where ε_r is the relative dielectric constant of the solvent, Φ is the surface potential, z_i is the valency of the counter-ions and c_{io}^* is the ion concentration in the bulk solvent. There is no exact analytical solution for the PB equation except for some special cases. In the limit of low surface potential ($|ze\Phi| < kT$), the PB equation can be linearized (Debye-Hückel) to,

$$\varepsilon_o \varepsilon_r \nabla^2 \Phi = - \left(\sum_i z_i e c_{io}^* - \sum_i \frac{z_i^2 e^2 c_{io}^*}{kT} + \dots \right) \quad (2)$$

The first term on the right side of the equation can be eliminated due to charge neutrality in the solution, thereby giving,

$$\nabla^2 \Phi = \kappa^2 \Phi \quad (3)$$

where κ is the inverse Debye length given by ,

$$\frac{1}{\kappa} = \left(\frac{\epsilon_o \epsilon_r kT}{\sum_i (z_i e)^2 c_{io}^*} \right)^{1/2} \quad (4)$$

For 1:1 electrolyte in aqueous solvent at 25 °C,

$$\frac{1}{\kappa} = 0.304 / c_o^{1/2} \quad (\text{nm}) \quad (5)$$

In order to solve equation (1), suitable boundary conditions have to be applied. For example, the following can be used,

$$\left. \frac{d^2 \Phi}{dz^2} \right|_{z \rightarrow \infty} = 0 \quad (6)$$

$$\left. \frac{d^2 \Phi}{dz^2} \right|_{z=0} = \frac{-\sigma}{\epsilon_o \epsilon_r} \quad (7)$$

Equation (6) and (7) describe the 1D potential in the solvent and at the surface respectively. This is valid for an infinite planar surface with a uniform surface charge density, σ . After applying these boundary conditions to equation (3), the solution for the potential becomes,

$$\Phi(z) = \Phi_o \exp(-\kappa z) \quad (8)$$

$$\Phi_o = \frac{\sigma}{\epsilon_o \epsilon_r \kappa} \quad (9)$$

For a sphere of radius a ,

$$\Phi = \frac{a\Phi_o}{r} \exp[-\kappa(r-a)] \quad (10)$$

$$\Phi_o = \frac{a\sigma}{\epsilon_o\epsilon_r(1+\kappa a)} \quad (11)$$

where r is the distance from the center of the sphere. In this geometry, the electrostatic potential decays exponentially with distance. At a distance from the surface equal to $1/\kappa$, the potential falls by a factor of $1/e$ (or 36.8 %) and the number of counterions in the diffuse double layer decreases by an even larger fraction: which justifies the designation of $1/\kappa$ as the “thickness” of the double layer. One of the factors that affect the Debye length is the ionic strength of the solvent (equivalent to the counter-ion concentration). This can be seen from Fig. 2.2 below.

Fig. 2.2 The effect of ionic strength on the range of the electrostatic interaction. Higher ionic strength increases the effect of screening and limits the range of interaction of the electrostatic forces.

Another case to solve the PB equation is for symmetrical z - z electrolyte. In this case, equation (1) reduces to,

$$\varepsilon_o \varepsilon_r \nabla^2 \Phi = -2ze n_o \sinh\left(-\frac{ze\Phi}{kT}\right) \quad (12)$$

with no restriction on the surface potential. Equation (12) has been solved analytically only for planar surface, where the solution for the PB equation is given as

$$\Phi(z) = \frac{2kT}{ze} \ln \left\{ \frac{1 + \Gamma_o \exp(-\kappa z)}{1 + \Gamma_o \exp(-\kappa z)} \right\} \quad (13)$$

where,

$$\Gamma_o = \frac{\exp(ze\Phi_o/2kT) - 1}{\exp(ze\Phi_o/2kT) + 1} = \tanh\left(\frac{ze\Phi_o}{4kT}\right) \quad (14)$$

The charge density in this case is given by,

$$\sigma = \left(8kTc_o^* \varepsilon_o \varepsilon_r\right)^{1/2} \sinh\left(\frac{ze\Phi_o}{2kT}\right) \quad (15)$$

The inadequacies of the Guoy-Chapman (GC) theory become evident when observations of the properties of electrode surface in solution are made. For example, the measured capacitance at the mercury/solution interface is lower than that predicted by the GC theory. The source of this difference is attributed to the neglect of the finite size of the counter-ions near the charged surface i.e. point-like particles. Stern [19]

introduced ionic dimensions into the model of the double layer for its inner localized portion (the Stern layer), thereby creating a theory based on the combination of the Helmholtz and GC theory. The Stern layer is within the plane of shear (Fig.2.3) so it moves with the particle when the particle is moving with respect to its medium. The total surface potential Φ_o is divided into a potential drop Φ_s over the diffuse part of the double layer and a potential drop, $\Phi_o - \Phi_s$ over the Stern layer. The GC theory applies without change to the diffuse part of the double layer, which begins from the Stern layer. The potential, Φ_s is equivalent to the zeta potential, ζ , which can be measured experimentally by electrophoresis techniques. Thus, it is convenient during calculation of the net interaction forces to set the surface potential as the measured zeta potential. In this way, the calculated potential should fit the actual practical potential reasonably well. This eliminates some of the experimental discrepancies with theory in the measurement of the surface potential.

Fig. 2.3 Stern version of the counter-ions distribution in the solution. The fixed Stern layer causes a potential drop from the actual surface potential. Beyond the Stern layer, GC theory can be used to calculate the potential drop.

The easiest way to measure the zeta potential of dispersed particles is by electrophoresis where an electric field is applied across a suspension of colloidal particles [21]. The motion of the particle under the influence of the electric field can be measured and the particle mobility can be used to calculate the zeta potential. The equipment used to measure this property is a ZetaPlus zeta potential analyzer from Brookhaven Instrument Corporation. In ZetaPlus, Laser Doppler Velocimetry method

is used to measure the particle velocity, and in turn, the particle mobility. In order to convert the velocity to zeta potential, the Smoluchowski equation can be used [19],

$$\zeta = \frac{\eta v}{\varepsilon_o \varepsilon_r E} \quad (16)$$

where η is the viscosity of the solvent, v is the velocity and E is the applied electric field. This equation is valid for solution with high ionic strength. Alternatively, in a solvent with low ionic strength, Hückel derived the equation for zeta potential [19],

$$\zeta = \frac{3\eta v}{2\varepsilon_o \varepsilon_r E} \quad (17)$$

where a factor of 3/2 is added in front of the Smoluchowski equation to compensate for low ionic strength. With the measured zeta potential, it is possible to plug in the right value in the equations to get the electrostatic potential dependence of charged surface in a polar solution. After obtaining the quantitative form for the electrostatic potential, the interaction potential between two surfaces can be derived.

The difficulty in obtaining the interaction potential between two surfaces is due to the difficulty to obtain the potential drop across the solution when two double layers overlap. In a simple case, the potential drop can be estimated as the sum of the potential drop of the two interacting surfaces. Then, the electrostatic repulsive potential between two spherical particles can be obtained as,

$$V_R = \frac{64c_o \Gamma_o^2 kT}{\kappa} \exp(-\kappa r) \quad (18)$$

So far, the discussion on the electrostatic potential is adequate to help in the understanding of the DLVO potential. However, more sophisticated theory has been developed to refine the understanding and help to explain some experimental anomalies observed with more advanced instruments. For most practical applications and our experiments, the discussed theory is adequate. The second force in the DLVO model is the Van der Waals' force which will be described next.

2.3 Van der Waals' Force

The first analysis of the attractive forces between molecules was first done by London [18]. In the simple model for an atom or molecule, the electron cloud distribution can be polarized by the presence of the electric fields to form dipoles. Thus, at high temperature, the fluctuation in the electron cloud can induce a dipole to form in adjacent molecules which in turn interact with the original molecule to induce a dipole. Based on an induced dipole-induced dipole interaction, the attractive potential between two molecules is given by,

$$\phi_{12}^d(r_{12}) = -\frac{3}{2} \left(\frac{h\nu_1 h\nu_2}{h\nu_1 + h\nu_2} \right) \frac{\alpha_1 \alpha_2}{r_{12}^6} = -\frac{C_{12}}{r_{12}^6} \quad (19)$$

where $h\nu$ is the characteristic energy of a molecule approximately equal to the ionization energy, α is the polarizability and r_{12} is the intermolecular distance. The

London constant, C_{12} is a constant to quantify the interaction of two different materials as indicated by the subscripts 1 and 2.

The forces of attraction between particles can then be calculated by summing the London force between all pairs of molecules in the separate particles. This method is pioneered by Hamaker [18]. The effect of the summation of the London forces can be captured by using the Hamaker constant,

$$A_{12} = \pi^2 C_{12} \rho_1 \rho_2 \quad (20)$$

The Hamaker constant encompasses the material-dependent part of the attractive forces. Taking account of the geometry of the system, the Hamaker constant can then be inserted into a suitable equation to be used to calculate the Van der Waals' forces. In the case of two spherical particles, the Derjaguin [19] approximation can be used.

Fig 2.4 Schematic showing the geometry considered in the Derjaguin approximation.

Assume that we have two large spheres of radii R_1 and R_2 at a small distance D apart (Fig. 2.4). The attractive force, F , can be obtained by integrating the force between the two circular regions of area $2\pi x dx$ on one surface and the opposite surface, which is assumed to be locally flat and at a distance $Z = D + z_1 + z_2$ away. The net force becomes

$$F(D) = \int_{Z=D}^{Z=\infty} 2\pi x dx f(Z) \quad (21)$$

where $f(Z)$ is the normal force per unit area between the two surfaces. Since from Chord theorem $x^2 \approx 2R_1 z_1 = 2R_2 z_2$, we have

$$Z = D + z_1 + z_2 = D + \frac{x^2}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (22)$$

$$dZ = \left(\frac{1}{R_1} + \frac{1}{R_2} \right) x dx \quad (23)$$

so the force becomes

$$F(D) = \int_D^\infty 2\pi \left(\frac{R_1 R_2}{R_1 + R_2} \right) f(Z) dZ \quad (24)$$

The potential due to the attractive Van der Waals' forces can then be derived for two spheres as

$$V = -\frac{A_{12}}{6r} \frac{a_1 a_2}{(a_1 + a_2)} \quad (25)$$

where a_1 and a_2 are the radius of the two spheres. If it is the dispersion force that is of interest, the effect of the intervening medium has to be taken into account. This can be accounted for by modifying the Hamaker constant as follow

$$A_{132} = A_{12} + A_{33} - A_{13} - A_{32} \quad (26)$$

The subscripts of the Hamaker constant refer the combination of materials used. For example, A_{132} refers to a pair consisting material 1 and 2 with a medium 3 between them.

The Hamaker constant for some materials is given in the Table 2.1 below.

Material	M Air M	M Water M
Water	3.7	0.0
Alkanes n = 5	3.8	0.3
n = 6	4.1	0.4
n = 10	4.8	0.5
n = 14	5.1	0.5
n = 16	5.2	0.5
Fused quartz	6.5	0.8
Fused silica	6.6	0.8
Sapphire	16.0	5.0
Polymethyl methacrylate	7.1	1.1
Polystyrene	6.6	1.0
Polyisoprene	6.0	0.7
Polytetrafluoroethylene	3.8	0.3
Mica	10.0	2.1

Table 2.1 Values of Hamaker constant ($\times 10^{-20}$ J) for some common combinations of materials M across air and water.

For geometries other than two spheres, the attractive forces can be calculated by inserting the material-dependent Hamaker constant into an expression for the corresponding geometry. Some examples of the expressions for common geometries are given in Fig. 2.5.

Fig. 2.5 Expressions to calculate the Van der Waals' forces for different geometries [18].

The Hamaker method of summation is a molecular method which starts from molecular-pair-wise interactions and scales up to the attraction between particles,

making various simplifying assumptions. An alternative approach is to start with the electrical properties of a particle and derive the dispersion forces directly. Landau and coworkers [18] pioneered this method based on the premise that the frequency dependence of the dielectric constant of a solid or liquid is related to the fluctuation of the electronic clouds of the whole material. The mathematics of Landau theory is daunting and beyond the scope of our study. However, the modification can be captured in the Hamaker constant,

$$A_{132} = \frac{3kT}{2} \sum_{n=0} \sum_{s=1} \left[\frac{\varepsilon_1(i\xi_n) - \varepsilon_3(i\xi_n)}{\varepsilon_1(i\xi_n) + \varepsilon_3(i\xi_n)} \right]^s \left[\frac{\varepsilon_2(i\xi_n) - \varepsilon_3(i\xi_n)}{\varepsilon_2(i\xi_n) + \varepsilon_3(i\xi_n)} \right]^s / s^3 \quad (27)$$

$$\varepsilon(i\xi) = \varepsilon_o \left(1 + \frac{2}{\pi} \int_0^\infty \frac{x \varepsilon_r''(x) dx}{x^2 + \xi^2} \right) \quad (28)$$

By using the modified Hamaker constant A_{132} in the calculation, more accurate results for the Van der Waals' forces can be obtained.

2.4 DLVO potential

As mentioned in the introduction, the DLVO potential is the sum of the electrostatic repulsive forces and Van der Waals' attractive forces. For two similar spheres, an expression can be given to describe the total potential,

$$V_{DLVO} = \frac{64c_o \Gamma_o^2 kT}{\kappa} \exp(-\kappa r) - \frac{A_{12}}{6r} \frac{a_1 a_2}{(a_1 + a_2)} \quad (29)$$

A schematic plot of the DLVO potential is shown to illustrate some of its features in Fig. 2.6.

Fig. 2.6 Schematic of interaction energy vs distance profiles of DLVO interaction. (a) Surfaces repel strongly: small colloidal particles remain dispersed. (b) Surfaces come to stable equilibrium at secondary minimum if it is deep enough: colloids remain 'kinetically' stable. (c) Surfaces come into secondary minimum; colloids coagulate slowly. (d) The 'critical coagulation concentration'. Surfaces remain at secondary or primary minimum; colloids coagulate rapidly. (e) Surfaces and colloids coalesce rapidly.

Firstly, there is a primary minimum near the particle surface. This is the reason for the observation of irreversible agglomeration in colloidal suspension and this happens when the particle separation is at the primary minimum. Another feature of the DLVO potential is the energy barrier at intermediate distances away from the particle surface. When the magnitude of the barrier is larger than thermal energy, it means that the colloidal particles in a dilute suspension are not able to overcome this barrier to

coagulate. This explains the stability of colloidal suspensions. There are two factors which can affect the magnitude of the energy barrier, as can be seen from the schematic. With increasing salt concentration or decreasing surface potential, it is possible for the barrier to completely disappear. The effect of salt concentration can be seen from Fig. 2.6 and 2.7. In this case, the increased ionic strength screens the surface charges and reduces the range of the electrostatic interactions. A third and most interesting feature of the DLVO potential is the presence of a secondary minimum beyond the energy barrier under certain conditions. This minimum presents an opportunity for the colloidal particles to assemble. When the depth of the secondary minimum is sufficient to overcome the thermal energy, an ordered structure will be able to form against the randomizing forces (Brownian). However, due to its shallowness, the coagulation can be easily reversed by some mechanical agitation. An interesting way to look at the self assembly process is by looking at the average separation between the particles at different stages of the process. For example, at low volume fraction, the average distance between the particles are far at the right side of DLVO potential (Fig. 2.6) and effectively, they do not feel any strong forces from each other.

Fig. 2.7 Irreversible agglomeration in colloidal suspension. The suspensions are similar except for the ionic strength. The ionic strength is increasing from 1 mM to 1 M (from left to right). At high ionic strength, the particles form disordered aggregates.

The DLVO theory is adequate to describe the interaction potential between charged colloidal particles which are the most commonly encountered system for aqueous suspensions. There is another method to stabilize colloid suspension known as steric stabilization. In such systems, surfactant molecules with long tails are adsorbed or polymer chains are grafted onto the surface of the colloidal particles. The added molecules on the surface uncoil themselves in the solvent, making the surface of the particles “hairy”. When the particles come into close proximity, the surfactants or chains on the surface overlap and prevent the particles from agglomerating. This is understood to be due to the entropic penalty that arises when the polymer chains are compressed. So far, there is no accepted quantitative theory for the interactions in steric stabilized systems. In our case, we are mainly concerned with the charge stabilized suspension as this is the system that is used in our experiments. Thus, the DLVO theory is adequate to help in our explanations of the phenomena observed in our experiments.

2.5 Ordering in Colloidal Suspension

Most theoretical and experimental work on phase behavior of colloidal suspension has been concentrated on model hard sphere suspension. In the hard sphere suspensions, the interaction between particles is eliminated and crystallization occurs at high concentrations. The way to eliminate the interaction forces is to use steric-stabilized particles in an index-matched solvent. Steric stabilization eliminates the electrostatic repulsion as the end groups of the polymer chains are typically uncharged. The polymer chains uncoil to a length of a few nms in solvent which can be ignored for micro-sized particles. The solvent is index-matched to the particle in order to eliminate the Van der Waals' forces. The reason for stability of ordered structure is that the particles gain entropy by arranging themselves on a lattice to maximize interparticle distance and the local free volume. Experimentally, the crystallization of a hard sphere suspension is described in work by Pusey and van Megen [22]. (Fig. 2.8) One observation in the hard sphere suspensions is that they crystallize at high volume fraction. Initially, the crystal structure of the hard sphere system is not clearly known. Both HCP and FCC are believed to be equally likely to be the equilibrium structure. However, this is resolved by calculation of the entropy difference between the FCC and HCP structure by Woodcock [23]. It is found that the FCC structure is more stable than the HCP structure by a significant free-energy difference $0.006kT$. The threshold volume fraction for crystallization has been found to be between ~ 0.49 to ~ 0.56 [24].

Fig. 2.8 Hard sphere colloidal suspension at various volume fractions. The volume fraction of the suspensions is increasing from right to left in the top picture. Corresponding numbered arrows are indicated in the phase diagram below. [22]

In the case of the charge stabilized particles as compared to hard spheres, the situation is complicated by the presence of interaction forces between the particles. Typically, it can be expected that the volume fraction for any crystallization should be lower than that of the hard sphere system. This is because the individual particles can feel the

influence of others at a range further than the hard sphere particles. It has also been shown experimentally that concentrated suspension of charge stabilized particles can form FCC structures [25, 26].

Fig. 2.9 Phase diagram of charged colloidal suspensions. The volume fraction, Φ is plotted against the ionic strength. It can be seen that the FCC structure occupies a large area of the phase diagram. [25] The range of ionic strength is relatively small (from 1.8 to 3.8 mM) and so there is no appreciable change in the volume fraction at which crystallization to FCC occurs.

The experimental phase diagram (Fig. 2.9) had been obtained by performing light diffraction experiments on the colloidal suspension at different volume fraction, Φ . In this case, a Kossel line analysis has been used to analyze the crystal structure [26]. It can be seen that the most stable crystal structure at high volume fraction is the FCC structure. Although the free energy difference between the FCC and HCP structure in a hard sphere system is relatively small, this can be significantly higher in a charged colloid suspension. This is because the only contribution to the free energy difference in hard sphere system is entropy, whereas there is enthalpy contribution due to the interaction forces in charged colloids. The extra contribution of enthalpy also causes

the charged colloidal suspension to exhibit non close-packed structure like BCC structure when the range of interaction extends beyond the nearest neighbors. In self assembly of colloidal particles, the colloidal suspension will go through a state of high volume fraction before drying up so it is valid to assume that the system will always go into the FCC phase field in the phase diagram. This provides an important theoretical basis on which the self assembly process can be analyzed in detail.

2.10 Synthesis of polystyrene colloids

After looking at the theoretical aspect of the colloidal interactions, it is natural to extend the discussion to the practical aspect of colloidal particle synthesis. This is an important step in the control of the particle surface functionalization, and in turn, the surface properties. Synthesis of colloidal particles is a diverse field by itself. It covers a large length scale from particle size of 10 μm down to a few nm and particles of various materials type like metals, polymers, ceramics and semiconductors. Quantum dots are examples of extremely small particle of semiconductors whose synthesis and stabilization are of intense research interest [1, 27]. For colloidal self assembly, two main types of particles are typically used. The first is silica colloids which are usually synthesized by a sol-gel method known as the Stöber process [28]. Silica particles are negatively charged when suspended in deionised (DI) water and sediment at a relatively high rate due to the high density of silica. The other type of particles is polymer particles with polystyrene particles as the most popular due to the ease of synthesis. The polystyrene colloids used in our experiments are synthesized by emulsion polymerization method [29]. In emulsion polymerization, the monomer is dispersed in water by creating an emulsion of the mixture and polymerized by suitable initiators. Special molecules known as surfactants are used to create the emulsion.

These molecules consist of a hydrophilic head group with a hydrophobic tail (Fig. 2.10 and 2.11). Surfactants are added into the reaction vessel and they are adsorbed onto the interface between the organic monomer and water. Above a certain concentration known as the Critical Micelle Concentration (CMC), the surfactant starts to form micelles around the monomer molecules. Micelles in aqueous solution are aggregates of surfactant molecules with the hydrophilic head in contact with surrounding solvent, sequestering the hydrophobic tail in the micelle centre. The monomer is stabilized and stay dispersed in water by the encapsulation in these micelles.

Fig. 2.10 Molecular structure of surfactant molecules. The top molecule is anionic Sodium dodecylsulfate, SDS. The bottom molecule is cationic Hexadecyltrimethylammonium bromide, CTAB. The image on the right is the structure of a micelle with blue ionic head group and red organic tail.

Fig. 2.11 Examples of free radical initiators used in the synthesis of polystyrene colloids. The top molecule is 2,2'-Azobis(2-methylpropionamidine) dihydrochloride which will produce positively charged particles. The bottom molecule is Potassium persulfate, KPS which will give negative particles.

In order to initiate the polymerization process, free radical initiators are added at elevated temperature. Highly mono-disperse polymer colloid particles can be synthesized in this way. However for our study, the added surfactants contribute to the concentration of counter-ions in the suspension and limit the range of ionic strength that can be achieved. Excess amount of the surfactant has also been added to ensure the stability of the monomer-water suspension. This is extremely difficult to remove in the final colloid suspension and typically reappear in the final colloidal crystal.

It is also possible to synthesize mono-disperse polymer colloid particles without added surfactant [30]. In this case, the monomer is dispersed in the water by mechanical agitation. A propeller is used to stir the suspension of monomer and water. At high revolution, the monomer will be broken into small droplet in water. Polymerization of the monomer can take place in the same way as emulsion polymerization. The obvious advantage of this method is the cleanliness of the colloid synthesized. However, particle size uniformity is more difficult to control in this method. Due to the requirement for low concentration of the impurities, we have chosen this method to synthesize our colloids despite the need for more effort to get uniform particles.

The monomer used for polystyrene polymerization was styrene. Initial washing of the styrene was done with 1 M sodium hydroxide solution. The two immiscible liquids were mixed in a separating funnel. The mixture was shaken vigorously to disperse the monomer in the NaOH solution and to remove the inhibitor added in the monomer by the manufacturer. The mixture was then left to stand for a while to separate the two liquids. The NaOH solution was removed from the separating funnel and the monomer was washed with DI water for another two times to remove the NaOH. The DI water was filtered with a Barnstead ion exchange system and had a resistivity of 18 MΩ.cm. This indicated that the water was ultra-pure.

After the monomer was cleaned, it was mixed with DI water in a reaction vessel and agitated with a Teflon propeller driven by an overhead stirrer as shown in Fig. 2.12. The reaction vessel was kept in a water bath and maintained at a temperature of 60 °C. At the same time, pure nitrogen was injected into the system. This was to provide a stable environment to stabilize the free radicals produced during polymerization and sustain the reaction. A condenser was also connected to the system to make sure that the evaporated reagents did not escape. After the system was left to stand for 30 minutes to completely purge the vessel of oxygen, the initiator was added to start the polymerization process.

The free radical initiator used in the synthesis was Potassium Persulfate (KPS). The choice of the initiator for the synthesis is very important as it determines the final surface properties of the colloids. Using KPS, the surface functional group will be a sulfate and this produces negatively charged particles. It is possible to use other kinds of initiators, such as amidine-type initiator to get particles with positive surface charge. In our experiments, we found that the negatively charged particles gave colloidal

crystals of higher quality. After the initiator was added, the system was continuously stirred and kept in nitrogen atmosphere for another 24 hours. The long standing time was to ensure that all the monomer had reacted. The resulting colloidal suspension was milky in color. After synthesis, the colloidal suspension was cleaned by centrifugation. The colloid particles sediment to the bottom after centrifugation, leaving a top layer of clear solvent which contained most of the ions and was poured away. DI water was added to the suspension and redispersed in an ultrasonic bath. This was repeated for a few times to ensure that the colloids suspension was clear of any leftover reagents. The amount of leftover reagents is related to the conductivity of suspension which can be easily measured experimentally. DI water has a conductivity of $\sim 0.1 \mu\text{S}/\text{cm}$ and a clean colloidal suspension will have a conductivity close to it.

Fig. 2.12 Schematic of the surfactant-free emulsion polymerization process. Monomer droplets are dispersed in water by mechanical agitation while initiators are added. After 24 hrs of reaction, mono-disperse particles will be produced.

Some of the physical properties were measured after synthesis. This included the volume fraction which was measured by Thermogravimetric Analysis (TGA). The weight loss of complete evaporation was obtained in TGA and volume fraction of the initial suspension was inferred from there. The zeta potential was also measured by the method mentioned earlier. Finally, the particle size and polydispersity of the colloids

were measured by checking the Scanning Electron Microscope (SEM) images of dried suspensions.

Chapter 3: Photonic Bandgap

3.1 1D, 2D and 3D Photonic Crystals

In a periodically structured electromagnetic media, there exists an interesting optical property known as the photonic bandgap (PBG) [31-33]. This is a band of electromagnetic radiation frequency that is forbidden to propagate in the structure. The periodicity, whose lengthscale is on the order of the wavelength of light in the bandgap, is the electromagnetic analogue of a crystalline atomic lattice. In an atomic system, the ion-core lattice acts on the electronic wavefunction to produce the familiar electronic bandgap. In PBG materials (or photonic crystals), the periodic dielectric modulation acts like a lattice for the electromagnetic waves to produce the bandgap. Similar to their atomic analogue, intentionally introduced defects in the PBG material can give rise to localized electromagnetic states which can act as linear waveguides and point-like cavities. PBG materials will be useful for future photonic circuits as they can act as a common platform on which photonic devices can be integrated.

Photonic crystals can be 1D, 2D or 3D, depending on the underlying symmetry and periodicity of the structure as shown in Fig. 3.1. 1D photonic crystals are commonly known as Bragg reflectors which are important technologically. They are used as UV reflective coating where the reflected band corresponds to the PBG. Omni-directional reflectors can be made from these structures and efficiency in lasers and optical fibers has been improved by the application of Bragg reflectors. With an added dimension, 2D photonic crystals can exhibit more exotic properties than their 1D counterpart and can potentially be important technologically. For example, superprism effect has been

observed in 2D photonic crystals [34] and self collimation is also achievable [35]. The reduction in the group velocity of light in 2D photonic crystals has been demonstrated experimentally [36] and this has huge potential for quantum computing. Overall, the importance of 1D and 2D photonic crystals is slowly being realized with advanced micro-machining. A major drawback of 1D and 2D photonic crystals is their inability to confine light in all dimensions.

Fig 3.1. 1D, 2D and 3D periodicity will create photonic bandgap of the corresponding spatial dimension.

For omni-directional confinement of light in all the spatial dimensions, 3D photonic crystal is clearly the best candidate. Technologically, this is also the ideal platform for integrated photonic circuits [37, 38]. Although it is possible to fabricate waveguide structures in 3D by combining a 2D photonic crystal with index guiding in the other direction, 3D confinement by PBG is expected to give the least loss which is important for practical applications. At the same time, point defects in 3D structures are expected to have extremely high Q factor which can help to achieve low threshold lasers. Finally, the slowing of light in the 3D photonic crystals means that detectors with high efficiency and improved photovoltaic devices can be fabricated. All these properties combine to give 3D photonic crystal more advantages over other technique to produce integrated photonic circuits.

3.2 Calculation of photonic bandgap

In our experiments, the PBG property of the structures has to be known to obtain information about the structures. In order to investigate detailed properties of the PBG, Maxwell's equations for electromagnetic waves have to be solved for a periodic dielectric medium. In solid state physics, the study of wave propagation in 3D periodic media was pioneered by Felix Bloch in 1928. Bloch proved that waves in such a medium can propagate without scattering, their behavior governed by a periodic envelope function multiplied by a planewave. The same technique can be applied to electromagnetic waves by casting Maxwell's equation as an eigenproblem similar to the Schrödinger's equation. By combining the source-free Faraday's and Ampere's law at a fixed frequency ω , one can obtain an equation in only the magnetic field, $\vec{H}$:

$$\vec{\nabla} \times \frac{1}{\varepsilon} \vec{\nabla} \times \vec{H} = \left(\frac{\omega}{c} \right)^2 \vec{H} \quad (30)$$

where ε is the dielectric function $\varepsilon(x,y,z)$ and c is the speed of light. This is an eigenvalue equation, with eigenvalue $(\omega/c)^2$ and an eigen-operator $\vec{\nabla} \times \frac{1}{\varepsilon} \vec{\nabla} \times$ that is Hermitian. In this form, the Maxwell's equation can be solved with the same linear-algebraic theorem used in quantum mechanics.

There are two common computational approaches to studying periodic dielectric structures: frequency-domain and time-domain. Each has its unique advantages and disadvantages. For frequency-domain methods, a direct computation of the eigenstates and eigenvalues of Maxwell's equations (usually using a planewave basis) is done. Each field computed has a definite frequency. In contrast, time-domain techniques

iterate Maxwell's equations in time; the computed fields have a definite time (at each time step) but not a definite frequency.

Time-domain methods are well-suited to computing things that involve evolution of the fields, such as transmission and resonance decay-time calculations. They can also be used to calculate band structures and for finding resonant modes, by looking for peaks in the Fourier transform of the system response to some input. The main advantage of this is that you get all the frequencies (peaks) at once from a calculation involving propagation of a single field. There are several disadvantages to this technique, however. Firstly, it is hard to be confident that you have found all of the states—you may have coupled weakly to some state by accident, or two states may be close in frequency and appear as a single peak; this is especially problematic in higher-order resonant-cavity and waveguide calculations. Secondly, in the Fourier transform, the frequency resolution is inversely related to the simulation time; to get 10 times the resolution you must run your simulation 10 times as long. Thirdly the time-step size must be proportional to the spatial-grid size for numerical stability; thus, if you double the spatial resolution, you must double the number of time steps (the length of your simulation), even if you are looking at states with the same frequency as before. Lastly, you only get the frequencies of the states; to get the eigenstates themselves (so that you can see what the modes look like and do calculations with them), you must run the simulation again, once for each state that you want, and for a time inversely proportional to the frequency-spacing between adjacent states (i.e. a long time for closely-spaced states).

In contrast, frequency-domain methods are in many ways better-suited to calculating band structures and eigenstates. Firstly, you do not have to worry about missing states—even closely-spaced modes will appear as two distinct eigenvalues in the result. Secondly, the error in the frequency in an iterative eigensolver typically decays exponentially with the number of iterations, so the number of iterations is logarithmic in the desired tolerance. Thirdly, the number of iterations typically remains almost constant even as you increase the resolution (the work for each iteration increases, of course, but that happens in time-domain too). Lastly, you get both the frequencies and the eigenstates at the same time, so you can look at the modes immediately (even closely-spaced ones). A traditional disadvantage of frequency-domain methods was that you had to compute all of the lowest eigenstates, up to the desired one, even if you didn't care about the lower ones.

In our case, we used software developed by S. G. Johnson and J. D. Joannopoulos from MIT which is freely available on the internet. The software is known as MIT Photonic Bandgap (MPB) and in it, fully-vectorial eigenmodes of Maxwell's equations with periodic boundary conditions were computed by preconditioned conjugate-gradient minimization of the block Rayleigh quotient in a planewave basis [39]. This software is a frequency domain method of calculation and is able to map the 3D PBG for various structures.

3.3 Photonic Bandgap of FCC structure

The FCC structure is one of the first to have its 3D PBG structure investigated. One of the requirements for full 3D PBG is a spherical Brillouin zone so that the band at all directions can easily overlap. Of all the common crystal structures, the FCC structure

has a Brillouin zone closest to being spherical (Fig. 3.2). Also, this is the equilibrium structure for colloidal crystals so it becomes important to look at the PBG properties of the FCC structure.

Using the MPB software it is possible to plot out the FCC PBG at the important symmetry points of the Brillouin zone.

Fig 3.2. The Brillouin zone for the FCC lattice. The important symmetry directions are shown in the diagram.

Fig. 3.3. The photonic band diagram of the FCC structure. It is calculated using MPB software for spheres with a dielectric constant of 2.53 in air. The bandgap at all the important symmetry points are shown.

Fig 3.3 above shows a typical band diagram of a FCC crystal made up of polystyrene spheres in air. The natural opal is also made up of silica particles arranged in a FCC structure and thus, the FCC structure is frequently referred to as an opal structure. From the band diagram, it can be easily seen that there is no full 3D bandgap up to band 15. This means that the opal structure is not the best candidate for a 3D PBG material. However, a full bandgap can be obtained by infiltrating the spaces between the particles with high dielectric index materials such as silicon. At the same time, in order to achieve a higher dielectric contrast, the original particles can be removed either by burning off or dissolution with a solvent. The final structure is known as the inverse opal structure.

Fig 3.4. The band diagram of an inverse opal structure of silicon. There is a full 3D PBG between band 8 and 9.

The band diagram of an inverse opal (Fig. 3.4) shows that there is a full 3D PBG between bands 8 and 9. This revelation has motivated substantial work on the infiltration of high index materials into colloidal crystal templates. However, there is still a strong need to produce high quality colloidal crystals with low defect density because it is likely that any change in the underlying template structure during infiltration and any incorporated defects will be present in the final inverse opal. The presence of defects in the structure can disrupt the properties of the PBG, especially in the high bands.

Experimentally, the easiest way to probe the PBG is by optical spectroscopy techniques like reflectance and transmittance measurement. Although there is no full 3D PBG in the FCC structure, it is still possible to observe a pseudo-gap at certain directions. This can be seen by zooming into a section of the band diagram of the FCC

structure (Γ -L point). In experiments, the presence of PBG will result in a peak and dip in the reflectance and transmittance spectra respectively. The central position of the peaks and dips can be predicted by taking the center of the bandgap, λ_{max} (band 2 and 3 for pseudo-gap in FCC). Alternatively, it is found that the position of the pseudo-gap can be predicted by a modified Bragg's law,

$$\lambda_{max} = 2d\sqrt{n^2(\lambda) - \sin^2 \theta} \quad (31)$$

where θ is the angle of incidence (with respect to $[111]$ direction) and $n(\lambda)$ is the effective refractive index. The spacing between each (111) plane is $d = 0.577a$, where a is the lattice parameter. The effective refractive index, $n(\lambda)$, is taken as,

$$n(\lambda) = n_{medium}(1 - f) + n_{colloid}(\lambda)f \quad (32)$$

where f is the packing fraction of the structure ($f=0.74$ for close packed structures). Thus, the peak wavelength is proportional to the lattice parameter of the FCC colloidal crystals in the same medium. In our experiments, both the modified Bragg's law and the MPB software are used to examine the expected position of the bandgap for the structures.

Chapter 4: In-situ PBG monitoring at the edge of sessile drop

Since it is known that the PBG is intimately linked to the structure, much information about the structure can be obtained by probing the PBG. This is especially helpful when in-situ PBG monitoring is implemented to check the structural change during the self assembly process. The initial experimental effort to make use of the PBG to monitor the colloidal self assembly process in-situ is carried out at the edge of a sessile drop of colloidal suspension [40]. The sessile drop configuration has a few merits that make it our first choice to attempt the study of the self assembly process. First of all, it is relatively easy to implement light spectroscopy experiments at the edge of a sessile drop. Spectroscopy components like light source and spectrometer are readily available off the market and easy to setup. Another merit is the static nature of the sessile drop edge. It is found that the meniscus at the edge of the sessile drop is pinned during the drying of the colloidal suspension [41]. With the pinned meniscus, the boundary from which a colloidal crystal assembles can be monitored without a need for a dynamic setup to follow the growth edge.

In the sections below, the experimental results are presented to help us to understand the self assembly process of colloidal particles. Firstly, the evolution of the meniscus during drying of a sessile drop of colloidal suspension is described with our experimental observation. The in-situ monitoring experiment will then be described and the corresponding structural changes during the self assembly process will be discussed. After that, the process of macroscopic cracking in the colloidal crystal will be investigated with low magnification optical images. Color changes during the

cracking process which is related to in-situ PBG changes will be used to infer the structural changes during the cracking process.

4.1 Meniscus boundary

As the self assembly of colloidal particles utilizes the drying meniscus edge as a boundary for assembling the colloidal particles into close-packed arrays, the meniscus plays an important role in determining the quality of the deposited film. Thus, the changes in the meniscus during drying are investigated in the beginning. The most common measure of the meniscus boundary is the contact angle. The equilibrium contact angle of a drop of solvent on a flat substrate is described by the Young's equation [18],

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (33)$$

where γ is the surface tension of the respective interface shown in the Fig. 4.1 below.

Fig 4.1. The three phase contact line at equilibrium.

In the case of the drop of colloidal suspension, the situation is more complicated due to the presence of the particles in the suspension. The problem is similar to “coffee-

drop deposit problem” which has been experimentally studied by a number of research groups where the evaporation of the sessile drops is being investigated. The most recent and complete experimental effort to date was conducted by Robert Deegan et al.[41-43]. They reported extensive results on ring formation and demonstrated that these could be quantitatively accounted for. It is observed that the contact line of a drop of colloidal suspension remains pinned during the drying process. While the highest evaporation occurs at the edges, the bulk of the solvent is concentrated closer to the center of the drop. In order to replenish the liquid removed by evaporation at the edge, a flow from the inner to the outer regions must exist inside the drop. This flow is capable of transporting the colloidal particles to the contact line and thus accounts for the higher local concentration of particles near the contact line (Fig. 4.2).

Fig. 4.2 The local volume fraction is increasing due to the solvent flux that transports particles to the edge of the drop. [41]

The deposit that remains after the solvent is dried off completely is ring-shaped due to this local increase in the solute content. Fig. 4.3 below shows a typical deposit left

behind after drying and Fig. 4.4 shows the side profile of the deposit. These dried deposits are observed under the SEM to be colloidal crystals.

Fig 4.3 Dark-field optical microscope image of the ring-shaped deposit in reflection. The white region is the deposit. Some particles are deposited in the central region of the drop as well but these are normally disordered monolayers.

Fig 4.4 The side profile of a dried sessile drop. It can be seen that there is an obvious accumulation of particles at the edge of the drop.

Ideally, the contact angle at which the solvent wets a surface will stay constant with a decreasing base width of the sessile drop because the system will try to stay in its equilibrium state as described by the Young's equation. However, in the case of a colloidal suspension, the contact line is pinned and the base width of the drop remains

constant. The pinning effect is due to the accumulation of particles at the drop edge. With the decrease in the volume of the solvent from drying, the contact angle has to decrease with time to compensate for the volume decrease (Fig. 4.5). Another observation is that as the initial volume fraction increases, the initial contact angle which the drop equilibrates to increases. This suggests that the pinning of the contact line is affected by the solid content in the suspension. It is likely that the colloidal particles that are transported to the meniscus edge attach themselves to the surface and prevent the solvent from spreading to its equilibrium base width. Despite the difference in the initial contact angle, the slope of the decrease in the contact angle with time is constant for the different suspension. Since the evaporation rate in the experiments are constant, this tells us that the decrease in the contact angle is simply a function of drying rate and not of the volume fraction. In our case, the relevant factor to consider is the constant increase in the local volume fraction at the drop edge and the decrease in the contact angle which forms a boundary to confine the colloidal crystal growth.

Fig 4.5 Plot of the changes in contact angle with time. Suspensions with different initial volume fraction are shown. A drop of DI water will ideally maintain its equilibrium contact angle at all time.

4.2 In-situ PBG changes and corresponding structural changes

In this part, the result of using the PBG to monitor the changes in the structure is described. With the pinned contact line, it becomes possible to perform spectroscopy experiments at the edge of the sessile drop with a static setup. The unique configuration in our setup allows us to observe the PBG changes during the self assembly process and relate the changes to the corresponding structural changes. The PBG is affected by the underlying structure and dielectric properties of the periodic structures. Usually, the dielectric properties of materials do not change with time. Thus, any changes in the PBG must be due to the structural changes. Reflectance spectroscopy is a common method to experimentally probe the photonic bandgap.

Incident light with wavelength within the PBG will be forbidden to propagate in the structure, registering as a peak in the reflected spectrum. We find that by following the PBG changes in-situ, we can infer the structural changes. This helps us to understand the mechanism and build a simple model for the self assembly process at the edge of a sessile drop of colloidal suspension. A schematic of the experimental setup is shown below in Fig. 4.6.

Fig 4.6 Schematic of the in-situ reflectance setup. The mirrors can be rotated to vary the incident angle onto the sample.

The light source used in the setup is a balanced light source (Deuterium-Tungsten halogen type) and coupled to the setup by an optical fiber (core diameter 200 μm). The light is deflected onto the edge of the drop by a series of mirrors which can be rotated to measure the reflectance spectra at various incident angles. The reflected light is collected with another similar optical fiber to a CCD array spectrometer with a grating which is optimized for the wavelength range of 300-800 nm. The whole setup is in a temperature controlled chamber to ensure constant evaporation rate.

The colloids used are polystyrene particles suspended in water. The diameter of the colloids is 180 nm with a zeta potential of -40 mV. The initial volume fraction of the

colloids is 0.023. The glass substrate on which colloid is deposited is an inert and colorless borosilicate glass cover slide. This substrate has no absorption in the visible range and constant light transmittance of 90% for wavelength of light between 350 and 750 nm as specified by the supplier.

A typical time evolution of the reflectance spectra is shown in Fig. 4.7. A few characteristics can be identified that help to reveal the mechanism of self assembly. Initially, after the drop is deposited on the substrate and stabilized, the reflectance spectrum shows no distinct peak. This indicates that the colloid suspension is dispersed with no long range structural order. This is consistent with the fluid-like structure in colloidal suspension that is expected at low volume fraction. The uniform scattering of light in a uniformly dispersed colloid suspension prevents a peak from appearing.

Fig 4.7 Reflectance spectra at the sessile drop edge at various intervals. The spectra are offset for clarity and share the same baseline.

As the drop dries up, a small peak starts to appear in the spectrum gradually. This peak can be attributed to the appearance of a PBG which is indicative of the presence of a periodic structure in the colloid suspension. The crystallization of colloidal crystals happens above a critical volume fraction and thus, the observed initial periodic structure is related to this volume fraction. Using a constant evaporation rate for a sessile drop, the volume fraction is calculated to be approximately 0.142. For a hard sphere system, the volume fraction for crystal formation is 0.494. In our case, the critical volume fraction is expected to be lower as the particles are interacting with each other. The initial colloidal crystal formed is expected to have a FCC structure as this is the lowest energy state. The validity of this assumption will be discussed in later sections using the variable angle results. On further drying, the initial peak shifts toward the shorter wavelength and increases in intensity. Finally, when the drop is totally dried up, the reflectance peak stabilizes at a fixed position. These observations will now be examined in detail to understand the processes that is happening.

For a FCC colloidal crystal, the position of the reflectance peak is related to the lattice parameter of the ordered structure. Thus, the observed changes in the reflectance spectra must be related to changes in the underlying structure. The modified Bragg's law can be used to estimate the central position of the PBG as mentioned earlier. In order to understand the self assembly process, the peak position is converted to lattice parameter using equation 31 and plotted against time in Fig. 4.8. Two distinct regions of evolution can then be seen in the plot. After the first appearance of an ordered structure, the lattice parameter shrinks at a gradual rate of 1.14 nm/min.

Fig. 4.8 Lattice parameter changes with time. During the first 92 minutes, no discernible peak is observed. The insets are schematics of the structural changes within the colloidal crystal.

The gradual decrease in the lattice parameter indicates that the lattice of the FCC structure is shrinking over time. This can be explained by the increasing influence of the liquid-vapor interface on the colloidal crystal. At the edge of the drop, the contact angle is decreasing over time as the drop is drying up. This confines the colloids and reduces the Brownian motion of the colloids. As a result, the lattice spacing becomes smaller and the intensity of the reflected light also increases with less disorder in the structure. In Fig. 4.8, the most interesting feature is the sharp drop in the peak position just before the colloidal crystal is totally dried up. This sharp drop indicates that there is a sudden decrease in the lattice parameter at the end of ordering in CSA. In order to quantify the change in the lattice parameter, the in-situ reflectance spectrum is taken at different angles of incidence. This allows for the delineation of the effect of the change

of the medium from water to air and the effect of the lattice parameter change. This can be seen by rearranging the modified Bragg's law.

$$\lambda^2 = 4d^2[n^2(\lambda) - \sin^2 \theta] \quad (34)$$

Thus, if the plot of λ^2 against $\sin^2 \theta$ is a straight line, the slope of the line can be used to obtain the lattice parameter. Fig. 4.9 shows the plot of the results. It can be seen that throughout the assembly process, the modified Bragg's law is obeyed and it shows that the FCC structure is maintained throughout. From the slope of the two straight lines, the lattice parameter at before and after the transition is obtained. The change in lattice parameter is 23.17 nm and this corresponds to shrinkage of 16.46 nm for each pair of colloidal particle. This is equivalent to a rate of 23.17 nm/min which is an abrupt decrease in lattice parameter relative to the initial rate of decrease.

Fig. 4.9 The plot of λ^2 against $\sin^2 \theta$. ▲: 10 minutes before abrupt transition ◆: Immediately before transition ■: After transition. Notice that the points fit onto a straight line, indicating that the structure stays FCC throughout the transition. All lines have different slopes.

This abrupt decrease in the lattice parameter is calculated to be approximately equivalent to the Debye screening length of 7.9 nm for the colloid suspension used. This suggests that prior to the final drying; the particles are prevented from coming into direct contact by the diffuse electric double layer of counter-ions. The colloidal crystal will stay in this metastable state as long as there is solvent around it to support the double layer. However, the solvent will eventually be removed by further evaporation and the diffuse layer of counterions cannot be sustained. This is an abrupt process and the sharp drop in the lattice spacing is the result of this. During this transformation, no diffusion of the colloids occurs and it is extremely fast relative to the time scale of the colloid motion. This transformation results in a dilatational lattice distortion of the transition state. Thus the final disappearance of the screening layer

corresponding to the change in surface medium gives rise to a global shrinkage that could exert shock stresses on the crystal, given its short time-scale. This, we believe, is responsible for the inevitable cracking in colloidal crystals grown using capillary forces of the meniscus.

4.3 Cracking of colloidal crystal

In our experiments, the presence of macroscopic cracks in self assembled colloidal crystals is consistently observed. These cracks tend to form perpendicularly to the drying front from the edge of the sessile drop. In order to help us understand the formation of these cracks, the in-situ formation of the cracks is observed under the optical microscope. An example of the observed changes is shown in Fig. 4.10 below. Initially, after the sessile drop has stabilized, it has a uniform dark color. This is consistent with the in-situ reflectance result in that no ordering has taken place in the initial stages. After about 15 minutes, a light blue region starts to form from the edge of the drying drop and it widens as the drop dries further. It is likely that this is an ordered region of colloidal crystal as reflectance measurements done on the dried colloidal crystal region indicates that the photonic bandgap lies in the blue region. This light blue region continues to widen until after another 20 minutes, cracks start to form spontaneously in the region. These cracks start from the edge of the drying drop and grow perpendicularly to the drying front. This suggests that stress is building up in the light blue region and crack formation acts as a stress relief mechanism.

Fig. 4.10 Optical images show the cracking process. The sequence of the images starts from the left to the right.

The origin of the stresses in the blue region is likely due to the shrinkage in the lattice parameter associated with the collapse of the electric double layer in the transition structure. SEM images of the cracks (Fig. 4.11) shows that the regions on each side of the cracks are oriented similarly. This suggests that the structure is ordered prior to cracking, further supporting that the cracking occurs at the transition state. This can be seen from Fig. 4.12 where the SEM image is processed by Delaunay triangulation for clarity. The vertices of the triangles are the center of each particle in Fig. 4.11. Two larger bold triangles are added to highlight the orientation relationship on both side of the crack.

Fig 4.11 SEM image showing the local order around a crack.

Fig. 4.12 The local order around the crack becomes more obvious after performing a triangulation scheme on Fig. 4.11. Each vertex of the triangles represents a particle. The bold triangle on both sides of the crack indicates that the colloidal crystals have similar orientation on both sides.

With the results so far, the process of colloidal self assembly at the edge of sessile drop can be seen as a two stage process. In the first stage, when the local volume

fraction gets sufficiently high, the interaction forces act on the particles and order them spontaneously. This is a thermodynamically driven process where the initial fluid-like structure crystallizes to a FCC structure with an enlarged lattice parameter. At this point, defects like vacancies and dislocation can be present in the structure, similar to atomic systems. They are expected to thermodynamically settle to an equilibrium concentration given sufficient time. This will be discussed in a later section. The structure of the FCC colloidal crystal is found to have a larger lattice parameter than expected and this is attributed to the presence of a double layer preventing the particles from coming into direct contact. In the second stage of self assembly, capillary forces must start to act on the structure as the liquid-vapor interface starts to close in the structure towards the end of drying. This causes the transition structure to go through an abrupt decrease in the lattice parameter as the double layer is removed on further drying. This observation and some indirect evidence have been used to explain the appearance of cracks that are consistently observed in self-assembled colloidal crystals. This concludes the experiment done on the sessile drop configuration and the next sections will be on results of similar experiments on another configuration.

Chapter 5: In-situ PBG changes during vertical deposition

The initial work on the in-situ PBG changes at the edge of sessile drop has proven to be rich in information about the structural changes during self assembly. It becomes natural to extend the idea of using PBG changes to other configurations of self assembly. In particular, it will be more relevant to adapt the idea to track the structural changes in a vertical configuration which is usually known as vertical deposition. In this configuration, the substrate is vertically submerged in the colloidal suspension. Due to wetting of the substrate by the suspension, there is a meniscus rise on the substrate. When the solvent in the suspension is allowed to evaporate off, a thin colloidal crystal film will be deposited at the trailing edge of the receding meniscus. Vertical deposition has proven to be a highly effective and easy method to obtain colloidal crystal films of uniform thickness. In comparison, the curved meniscus boundary in the drop configuration typically affects the macroscopic quality of the colloidal crystal and the thickness is not uniform due to the geometry of the meniscus boundary. Thus, vertical deposition has been the preferred method to grow large areas of colloidal crystals. Some variation of the method has also been demonstrated. For example, instead of making use of natural evaporation to recede the meniscus, the substrate can be drawn mechanically from the suspension. Another variation is the constant removal of the suspension fluid from the container by a peristaltic pump, resulting in a constant recession of the meniscus [44].

5.1 Meniscus Boundary

A few differences in the meniscus boundary exist between the vertical and sessile drop configuration. Firstly, the macroscopic curvature of the meniscus with respect to the substrate is different. At the edge of the sessile drop, the meniscus is convex, whereas the meniscus is concave at the region of meniscus rise on the vertical substrate. The second difference is the relative motion of the meniscus. In the case of the sessile drop, the meniscus is pinned due to the presence of particles in the suspension. However, in the vertical configuration, gravity causes the meniscus to recede as the level of suspension is decreased. This is an important difference in the characteristics of the two processes: static boundary in the sessile drop and moving boundary in the vertical case. These differences are the reasons for the capability to obtain colloidal crystal with uniform thickness in the vertical configuration. The role of the boundary will be discussed in greater detail in later sections.

There are several problems which complicates the adaptation of the optical spectroscopy setup for vertical deposition. Firstly, as mentioned previously, the meniscus is moving across the substrate. It is technically difficult to build a setup to follow the moving boundary with off-the-shelf components. Additionally, there is a line of sight problem for the light path. The deposition process must be carried out in a suitable container. The meniscus on the additional surfaces of the wall of the container will block the light path and prevents us from probing simply the substrate-meniscus region of interest. A third related problem is the deposition of colloidal crystals on the container wall. This will again present a line of sight problem when we try to probe the meniscus at the substrate.

There are various ways to overcome the problems. For us, the solution chosen is a relatively simple one. Firstly, instead of building a system to follow the moving meniscus, we decided to fix the light spot at an intermediate position below the initial meniscus position. By allowing the meniscus to sweep across the light spot, this is analogous to scanning across the different sections of the meniscus region. It is reasonable to expect the whole assembly process to occur within the meniscus region as the starting colloidal suspension is in a state where the fluid phase is in equilibrium. The geometry at the meniscus produces a force on the particles towards the substrate to adhere to it. Thus, by scanning the different meniscus sections, it is possible to capture the whole self assembly process and overcome the moving boundary problem. Despite solving the first problem, the line of sight problem is still present. From our experiments, it is found that colloidal crystals do not deposit on some surfaces like polymers. The reason for this will be discussed in the later sections of the report. Polymer cuvettes are commonly used to perform optical spectroscopy experiment on liquid samples like colloidal suspension and polymer blends. An additional characteristic of the polymer surface is that it is more hydrophobic than glass surface. Thus, the meniscus rise on a polymer surface is typically less than that on a glass surface. Combining these characteristics, it is possible to design a unique sample cell to perform the vertical deposition process and track the PBG changes at the same time.

A polymer cuvette is used as the container for the sample cell. A glass substrate is then fixed onto one of the walls of the cuvette. Optically clear glue is used as adhesive to fix the glass substrate. In this way, no colloidal suspension can seep into the space between the container wall and the back of the substrate. Otherwise, a thin layer of colloidal suspension will form between the wall and the back of substrate and

introduce an unwanted signal as it acts like a confined layer of colloidal suspension, where crystallization can take place. Studies by other groups have also demonstrated that colloidal crystal can form in a confined geometry [45-47]. The optically clear glue ensures that there will be no absorption when the signal passes through it. The sample cell is oriented in such a way that the light will pass through the glue layer before the meniscus which minimizes any possible interruption of the optical signal from the glue. Due to the difference in the wettability of the surfaces, the meniscus on the glass substrate rises higher than the rest of the surfaces in the polymer cuvette. This solves the line of sight problem associated with the container wall. Finally, no colloidal crystal is deposited on the polymer container wall which allows us to position the light spot at an intermediate position. A schematic of the transmission setup is shown in Fig.5.1 and optical images in Fig.5.2 shows the difference in the meniscus rise.

Fig. 5.1 Schematic of the setup used. The suspension is allowed to evaporate in a plastic cuvette with a glass substrate on one side. Due to the difference in the wettability, the contact line is higher in the substrate and this provides a line of sight for the transmission studies. The whole setup is kept in a temperature controlled chamber.

Fig. 5.2 Optical images showing the actual difference in the meniscus rise in the sample holder. It can be seen on the right image that a layer of colloidal crystal has formed on the glass substrate.

5.2 Volume fraction

Similar to the sessile drop configuration, the changes in volume fraction of colloidal particles at the meniscus has to be analyzed to help in the understanding the changes in the structure. In the case of vertical deposition with evaporation, there is a solvent flux transporting the particles to the meniscus region (similar to the case of sessile drop), thereby increasing the local volume fraction at the meniscus. However due to the geometry of the system, there is gravitational force acting on the particles against the flux and counteract the increase in volume fraction. Thus, the effect of sedimentation of the particles has to be considered. Based on the balance of the Brownian and gravitational forces acting on the particles, a quantity can be used to estimate the effect of sedimentation. This is the Peclet number given by:

$$Pe = \frac{m_B g a}{kT} \quad (35)$$

$$m_B = \frac{4}{3}\pi a^3(\rho_s - \rho_l) \quad (36)$$

where m_B is the buoyant mass of a particle with radius a and g is the gravitational acceleration. For $Pe > 1$, the particles have the tendency to sediment with gravity while for $Pe < 1$, the particles has the tendency to stay suspended. In the case of non-sedimenting particles, when the solvent flux transports the particles to the meniscus region, the volume fraction increases locally over time.

Complications arise when we attempt to estimate the local volume fraction by using a model of flux transport. The meniscus is a liquid-vapor interface to confine the colloidal particles within the solvent phase. Particles which are transported to the meniscus can bounce off from the interface and reverse the forces acting on the particles. The effect of this interface is difficult to incorporate into the model to quantify the local volume fraction. However, it is still reasonable to assume that the local volume fraction at the interface is increasing with time. This will provide a driving force for crystallization of the colloidal particles.

5.3 In-situ Transmittance Measurement

In the case of vertical deposition, transmission spectroscopy is chosen to examine the PBG changes. The transmittance measurement is able to probe the whole slab of colloidal crystal, as compared to a few layers beyond the plane of incidence in the case of reflectance measurement. This is due to the requirement for the light to pass through the whole colloidal crystal for transmission. The components used are similar to those used in the reflectance setup except in this case; a new sample holder is custom-made

to guide the light through the sample cell. This is the sample holder is placed in a temperature-controlled chamber to ensure a stable evaporation rate.

Fig. 5.3 Transmission spectra showing the appearance of the Dip A (608 nm), B (491 nm) and C (462 nm). Evolution occurs from t_1 to t_5 . Two dips are observed in the process of self assembly at t_2 and t_4 . Schematic of the structural change is shown in Fig. 5.6. The baselines of the spectra are offset for clarity.

The time evolution of the transmission spectrum is shown in Fig 5.3. Initially, the experiment is set up such that the meniscus is above the light path. Here, the transmittance spectrum is near zero and featureless because of strong scattering due to the relatively high volume fraction of the colloidal suspension near the meniscus and long path length that the light has to pass through the container. As the volume fraction increases with evaporation, a small dip (Dip A) appears in the transmission

spectrum (Fig 5.3). This dip can be interpreted to be the first appearance of order in the colloidal suspension and is the first kinetic stage of ordering. At this stage, the driving force for ordering is the interaction forces between the particles. This happens when the average distance between the particles decreases (because of rising local volume fraction) to the point where the interaction forces are more significant compared to the randomizing Brownian forces. This is consistent with the prediction of the stability of ordered structure at high volume fraction which is the equilibrium state.

For the PBG comparison, the more accurate method of calculation with the MPB software is used. As mentioned in the introduction, The MPB is capable of calculating the PBG in all directions. Thus, it is important to establish the right reference direction for the comparison of the calculation with the experimentally obtained spectra. In the case of vertical deposition, it is consistently seen that the (111) plane is always parallel to the substrate. This observation is useful for us to establish the right reference direction to analyze the experiment results. The observation also raises the question of the effect of the substrate in the self assembly process. More discussion on the role of the substrate will be discussed in the later sections. However, a possible reason for the preference for an (111) orientation will be discussed here. As the particles (sulfate-polystyrene) and substrate (glass) are both negatively charged, the growing crystal will prefer to orient its close-packed plane to the flat substrate as the flat substrate is equivalent to another close-packed plane. The light that is incident normally is always in the [111] direction and thus, this provides the reference direction for the PBG comparison. The expected peak position with respect to the calculated separation between the spheres in the transition structure (for 195 nm particles) is plotted in Fig.

5.4. This can be used to obtain the double layer thickness around each particle which is equal to half the separation.

Fig. 5.4 Calculated central wavelength of the photonic bandgap at different lattice constant for a FCC colloidal crystal in water with light incident on the (111) plane. It is plotted against the average separation between the spheres for comparison with Fig 3. The colloidal particles are 195 nm polystyrene particles with a dielectric constant of 2.64. The vertical dashed vertical line denotes the separation equivalent to 2 Debye length. The equilibrium colloidal crystal in air has a central wavelength at 463 nm.

The position of Dip A corresponds to a FCC colloidal crystal with a lattice parameter (368 nm) larger than that expected for an equilibrium colloidal crystal (276 nm) of the 195 nm polystyrene particles used. This transition structure is stabilized by the interaction forces and thus, exhibits the feature of the interaction potential. Here, the energy barrier in the DLVO potential prevents the particles from coming into direct contact. In order to quantify the separation of the colloids in the transition structure, it is easier to describe the colloids with an additional layer of counter-ions or electric double layer preventing them from direct contact. The thickness of this double layer can be approximated to be the Debye length in the suspension. Comparison with the DLVO potential has shown that this is a good approximation. For the colloidal suspensions used in our experiments, the value of the Debye length is 32 nm. This is

used to calculate the central frequency of the photonic bandgap of the transition structure and found to correspond well with the wavelength of the observed dip A in the transmission spectrum. It is interesting to note here that the volume fraction for crystallization is ~ 0.37 which is lower than that of ideal hard spheres (~ 0.49). This observation of a kinetically stabilized stage of colloidal self assembly is a clear demonstration that ordering in colloidal crystals first appears in the suspension state, and can be solely attributed to the inter-particle interaction forces, in contrast to the conventional view that self assembly during vertical deposition is driven solely by capillary forces.

The importance of the capillary forces becomes evident after the solvent continues to be evaporated off. Previous work by Kralchevsky et al. [48-51] shows that for floating particles, lateral capillary forces are negligible for particles smaller than $10\text{ }\mu\text{m}$. Thus, the lateral capillary forces will not affect the transition structure in the first stage where the particles are floating at the meniscus, supporting the idea that the interaction forces are the dominant driving force there. However, at the thinning edge of the meniscus where the transition structure is compressed against the substrate by the meniscus, the floating particle model is no longer adequate so the immersion capillary forces become dominant. Physically, the lateral capillary forces are related to the local curvature of the meniscus at the contact line on the individual particles. Due to the confinement by the substrate, the local meniscus of partially submerged particles is more distorted than the floating particles, producing much stronger lateral capillary forces even for particles as small as 10 nm . In our case, the energy due to immersion capillary forces can increase to $\sim 10^5\text{ kT}$ for meniscus recession (beyond the top of the particles) as small as a few nm. This large capillary force is enough to overcome the

energy barrier present in the DLVO potential, ~ 15 kT in this case, bringing the particles into direct physical contact, thereby reaching an equilibrium state corresponding to the primary minimum of the DLVO potential curve. The calculated DLVO potential for a particle pair used in our experiments is shown in Fig. 5.5. Utilizing the insight into the relative magnitude of the forces, it is possible to propose the role of 2D capillary forces in the final 3D packing of the transition structure. The effect of this capillary force is first felt by the top layer of the transition structure. However, the abrupt collapse of the double layer around the particles in the top layers (because of forced physical contact) causes the counter-ions to diffuse downwards thus increasing the local ionic strength of the adjacent layers. This increase is enough to lower the energy barrier below the thermal energy and the adjacent layers below will also come into direct contact. The collapse of the double layer will cascade all the way down to the layers adjacent to the substrate, thereby creating a final equilibrium 3D structure of colloidal particles in direct contact with water in the interstices.

Fig. 5.5 The calculated DLVO potential of the colloidal suspension used in our experiments plotted against the separation between the spheres. The surface potential is taken as the measured zeta potential of -40 mV and ionic strength of 0.1 mM KCl. The dashed vertical line denotes the separation equivalent to 2 times the Debye length. The energy barrier has a magnitude of ~ 15 kT.

The collapse of the double layer manifests itself as an appearance of a second dip (dip B) at a shorter wavelength. The position of dip B corresponds to that of a FCC colloidal crystal with the colloidal particles in direct physical contact (zero separation) with water in the interstices. The interstices in the colloidal crystal can act as capillary pores and wick up the water even after the meniscus has receded past the colloidal crystal. This compensates for the expected further blue shift in the dip position due to the change in dielectric contrast which is not observed. The coexistence of the two dips in the transmission spectrum is due to the finite size of the aperture of the optical system which superimposes the 2 structures onto each other. Dip B continues to grow in intensity at the expense of Dip A as the area of collapsed colloidal crystal grows in size. Finally, it stabilizes for a long period of time because of the continued wicking of the solvent into the interstices for a long distance after the meniscus has receded. This corresponds to a second kinetic stage of colloidal self assembly, where strong lateral immersion capillary forces collapse the electric double layer, bringing particles into direct contact, with the solvent trapped in the interstices.

After the meniscus has receded far enough that the wicking action of the interstitials can no longer sustain the flow of solvent, final drying occurs. This stage appears as Dip C in Fig. 5.3, blueshifted in wavelength due to the increased dielectric contrast of the colloidal crystal when the water in the interstices is replaced by air. Dip C also grows at the expense of the Dip B for reasons of overlapped probing mentioned before. The width of the dip is also observed to be larger in the dry colloidal crystal due to the increased dielectric contrast and is consistent with the photonic bandgap calculation done. A schematic summarizing the structural changes with respect to the position of the meniscus is shown in Fig. 5.6.

Fig. 5.6 The self assembly process. At different points relative to the receding meniscus, different forces become dominant for ordering. A transition structure is observed with a lattice parameter larger than that of the equilibrium state. After the meniscus has receded, the interstitials wick the water up and gives rise to the second dip in the transmission spectra. Final colloidal crystal is formed after the wicking action cannot be sustained.

So far, our experimental results have helped to separate the dynamic process of self assembly in colloidal suspension into three distinct kinetic stages. In the first stage, interaction forces provide the driving force to assemble the structures. The second stage is dominated by capillary forces acting on the particles, enabling them to overcome the DLVO energy barrier and come into direct physical contact. At this stage, the wicking action of the interstices retains water in the interstices within the close-packed structure. Finally, when the wicking solvent flux is no longer able to compensate for the evaporative flux, the structure reaches its final structure, which is similar structurally to stage 2, except that the water in the interstices is replaced by air.

The relative stability of the transition structure in the second stage is investigated by injecting more solvent into the system after the structure appears. The results show that despite being submerged in more solvent, the structure remains stable. There is no increase in the lattice parameter as the meniscus creeps up when solvent is injected and subsequent withdrawal of the solvent yields the same dip position in the

transmission spectra. These observations show that once the particles have overcome the DLVO energy barrier and equilibrate at the primary minimum (with zero separation), the colloidal crystal is stable against capillary forces. This is beneficial for subsequent solution processing such as infiltration with other functional materials.

With the understanding of the different structural changes that the colloidal suspension goes through, it is possible to make use of the knowledge and engineer the process to control the quality of the colloidal crystals formed. In the next chapter, the effects of macroscopic boundary on the self assembly of colloidal particles will be presented.

Chapter 6: Macroscopic Boundary Effects

So far, the experimental results have been concentrated on the microscopic structural changes during the self assembly process. This has yielded rich information about the mechanism of self assembly. The understanding of the initial stage of self assembly has been based on the microscopic interaction forces acting in a coordinated manner to order the particles spontaneously. However, it is presumptuous for us to assume that the mechanism can be entirely explained by the microscopic forces alone. Instead, there is a strong effect from the macroscopic boundary acting on the self-assembling system.

Hence, this section of the thesis will be concentrated on some analysis on the effects of the macroscopic boundaries. In previous sections, some aspects of the action of the boundaries have been described. For example, in the vertical deposition case, it has been demonstrated the capillary forces act in a manner that is favorable for the stability of the colloidal crystal. The condition at the meniscus boundary is complicated in that it involves two distinctly different boundaries: the substrate on which the colloidal crystal will be deposited on, and the liquid-vapor interface between the solvent and the atmosphere. In the following two sections, the characteristics of the two surfaces and consequently, the effects on the self-assembling system will be discussed.

6.1 Substrate Boundary

The first characteristic of the substrate on which the particles are deposited is that it is typically rigid. It can either be planar or patterned. In order to simplify the analysis, planar substrate will be considered. There has been a strong interest in making use of patterned substrate to assemble colloidal particles [52-59]. However, the effect of templated growth will not be discussed here as it combines both the effect of confinement by substrate topography and capillary forces. The purpose of this discussion is to separate the two effects to understand the effect on a self-assembled structure. The rigid nature of the substrate means that any self-assembled structure has to follow the surface topography of the substrate. Another characteristic of the substrate is its surface charge density. The substrate can have positive, negative or neutral surface charges, depending on the surface functional groups. For example, the glass substrate used in our experiments are typically negatively charged. This is due to the dissociation of silanol groups when the glass (silica) surface is in contact with deionized water. The equation for the reaction is shown as follow:

The nature of the surface charge of the substrate is important as it can interact with the particles and affect the self assembly process adjacent to the substrate. This is especially true for charge-stabilized colloidal suspensions. In our experiments, it is found that it is easier to order the particles with similar surface charge as the substrate. The colloidal crystals have a well-ordered structure throughout its thickness. However, for particles that have a surface charge opposite to that of the substrate, the colloidal crystal typically has an adhesion problem which results in the top colloidal

crystal peeling off from the substrate. Interestingly, a disordered monolayer of colloidal particles is left over after the top crystal has peeled off. This can be seen from the SEM images of the substrate after deposition (Fig. 6.1). On the other hand, the SEM images of the top of the colloidal crystal shows an ordered structure. This conundrum can be resolved by looking at the role of the substrate in the model of self assembly that has been discussed in the earlier chapters. The formation of the colloidal crystal can occur without any interference from the substrate since it is the equilibrium structure. However, if there is a strong attractive force between the substrate and the particles, some of the particles will be randomly adsorbed onto the substrate, thereby forming a disordered monolayer. The lateral mobility of the adsorbed particles is relatively low due to the strong adhesion to the substrate. Even though well ordered colloidal crystals can be formed in the region away from the substrate, the bottom part of the colloidal crystal will become distorted when it comes into contact with the disordered monolayer at the substrate (Fig. 6.2). This produces a structure with a disordered bottom and an ordered top.

Fig. 6.1 Schematic showing the difference in the ordering on the top and bottom of colloidal crystals of positively charged particles on glass (negatively charged). SEM images show that the top is ordered whereas the bottom is not.

Fig. 6.2 The cause of the difference in order is the presence of an adsorbed monolayer of particles which is disordered. It frustrates the deposition of the colloidal crystal.

One assumption of the model is that the relative adhesion force of the particles on the substrate is strong enough to keep the monolayer disordered against the capillary forces. A simple experiment can be done to check the validity of the assumption. A glass substrate is dipped into a suspension of positively charged particles for a few minutes, and then dipped into DI water to wash away any excess particles. After the substrate is removed from the DI water and dried, the substrate is observed under the optical microscope. From Fig. 6.3, it can be seen that a monolayer of disordered particles is left on the substrate. This shows that the adhesion forces between the particles and the substrate can indeed overcome the strong capillary forces that are experienced by the adsorbed particles upon removal from the suspension. In other word, the particles adhere to the substrate so strongly that they cannot undergo any rearrangement to form an ordered monolayer.

Fig. 6.3 Optical image of the adsorbed monolayer of 300 nm positive particles on glass after taking out of the colloidal suspension.

After understanding the reason for the poor adhesion of the colloidal crystal of positive particles on glass, the idea can be extended to explain the relative ease of assembling negatively charged particles on glass. The electrostatic repulsion between the negative particles and glass substrate prevents the particles from adhering prematurely onto the substrate to form a disordered monolayer. However, there is no analytical solution for the Poisson-Boltzmann equation for the geometry of a particle near a substrate.

With the presence of the electrostatic repulsion from the substrate, an attractive force must exist that acts to hold the assembled colloidal crystal on the substrate. This force is the Van der Waals' force. In the same way that the Van der Waals' force provides the attractive force to hold the particles in a FCC structure, it helps to hold the assembled colloidal crystal on the substrate against the capillary forces. The attractive forces can be calculated by using the appropriate equation for the geometry of a particle near a surface and the right Hamaker constant. It can be seen from the plot below (Fig. 6.4) that the attractive forces of the particle-substrate system is stronger than the particle-particle system. However, it decreases extremely fast as separation increases. The magnitude of the total attractive Van der Waals' forces is additive, giving rise to large attractive forces when colloidal crystals consisting of many particles come into close proximity of the substrate. Thus, it is possible for the ordered colloidal crystal to adhere strongly to the substrate as there is a large density of particles in contact with the substrate and provides necessary adhesion forces. This also allows the deposited colloidal crystal to be reintroduced into a solvent environment without any peeling, thereby allowing subsequent wet processing steps like infiltration of active materials.

Fig. 6.4 Plot of Van der Waals' force for two geometries. The particles used for calculation are 195 nm polystyrene particles and the substrate is also polystyrene. The purpose is to illustrate the difference in the forces due to geometrical effects.

One important observation is that the FCC colloidal crystals will always orient the (111) plane parallel to the substrate. This can be expected for a planar substrate without any topography. In the case of a substrate with similar charge to the particles, the planar substrate appears as a close-packed (111) plane to the colloidal crystal. On the other hand, it is not true for a substrate of different charge and this can be seen from the disorder at the regions adjacent to the substrate as shown before.

6.2 Meniscus boundary

Compared to the substrate, the meniscus boundary is deformable and is dynamic due to the evaporation of the solvent from the suspension. On the other hand, there is no surface charge associated with meniscus which means that the electrostatic forces

between the interface and particles will be negligible. The most significant forces acting at the vapor-liquid interface are the capillary forces and thus, it is adequate to examine the effect of the meniscus boundary on the self assembly of the colloidal particles. Capillary forces are 2D forces acting in the plane of the meniscus boundary, meaning that they are highly directional as compared to the interaction forces between the particles. The problem of the capillary force acting between colloidal particles has been studied in great depth by Kralchevsky et al. [51] for 2D particle arrays and their results are summarized below.

The origin of the capillary force is deformation of the liquid surface, which is supposed to be flat in the absence of particles. The larger the interfacial deformation created by the particles, the stronger the capillary interaction between them. It is known that two similar particles floating on a liquid interface attract each other. This attraction arises because the meniscus deforms in such a way that the gravitational potential energy decreases when they approach each other. Hence the origin of this force is the particle weight. A force of capillary attraction appears also when the particles (instead of being freely floating) are partially immersed in a liquid layer on a substrate. The deformation of the liquid surface in this case is related to the wetting properties of the particle surface, i.e. to the position of the contact line and the magnitude of the contact angle, rather than to gravity. To distinguish the capillary forces in the case of floating particles from ones in the case of partially immersed flotation particles on a substrate, we call the former lateral forces and the latter lateral immersion forces as illustrated in Fig. 6.5. The forces can be attractive or repulsive depending on the slope of deformation.

Fig. 6.5 Various lateral capillary forces that can occur between pairs of particles

For the systems depicted in Fig. 6.5 (menisci decaying at infinity), letting $z = \zeta(x,y)$ be the equation of the deformed fluid surface and solving the Laplace equation of capillarity for small meniscus slope,

$$\nabla^2 \zeta = q^2 \zeta \quad (37)$$

in cylindrical coordinates (r, ϕ) , one can determine the interfacial shape around a single particle,

$$\zeta(r) = AK_0(qr) \quad (38)$$

where K_0 is the modified Bessel function of the second kind and zeroth order and A is a constant of integration,

$$\begin{aligned} q^2 &= \Delta\rho g / \sigma & (\text{for thick films}) \\ q^2 &= (-\Pi') / \sigma & (\text{for thin films}) \end{aligned} \quad (39)$$

Here σ is the density of the fluid, $\Delta\rho$ is the difference between the mass densities of the two fluids, g is the acceleration due to gravity and Π' is the derivative of the disjoining pressure with respect to the film thickness. Equation 38 describes a meniscus which is exponentially decaying at infinity. Furthermore, one can apply the superposition approximation, i.e. assume that the interfacial deformation caused by two particles is equal to the sum of the deformations caused by the separate particles in isolation. Then, in view of equation 38, the energy of lateral capillary interaction between the two particles is obtained in the form,

$$\Delta W \approx -2\pi\sigma Q_1 Q_2 K_0(qL) \quad (40)$$

where L denotes the distance between the centers of the two particles, $Q_i = r_i \sin\psi_i$ ($i=1,2$) are the so called ‘capillary charges’, r_i and ψ_i are the radii of the contact line and the slope angle at the contact line of the respective particle. ΔW represents a variation in the gravitational energy in case of flotation force, or in the energy of wetting in case of immersion force. The lateral capillary force is given by the derivative $F = -d\Delta W/dL$, which yields,

$$F \approx -2\pi\sigma Q_1 Q_2 q K_1(qL) \quad (41)$$

(K_1 - modified Bessel function). The asymptotic form of equation 41 for $qL < 1$ ($q^{-1} = 2.7$ mm for water),

$$F \approx -2\pi\sigma Q_1 Q_2 / L \quad (42)$$

looks like a two-dimensional analogue of Coulomb's law for the electric force. This is the reason for calling Q_1 and Q_2 'capillary charges'. Generally speaking, the capillary charge characterizes the local deviation of the meniscus shape from planarity at the three-phase contact line. The flotation and immersion capillary forces exhibit similar dependence on the interparticle separation, L , but very different dependencies on the particle radius and the surface tension of the liquid. The different physical origin of these forces results in different magnitudes of the corresponding 'capillary charges'. In this respect there is an analogy with the electrostatic and gravitational forces, which obey the same power law, but differ in the physical meaning and magnitude of the force constants (charges, masses). In this particular case, when $R_1 = R_2 = R$ and $r_k \ll L \ll q^{-1}$, one can derive,

$$\begin{aligned} F &\propto (R^6/\sigma) K_1(qL) && \text{for flotation force} \\ F &\propto \sigma R^2 K_1(qL) && \text{for immersion force} \end{aligned} \quad (43)$$

In other words, the flotation force decreases, while the immersion force increases, when the interfacial tension σ increases. Besides, the flotation force decreases with the decrease of R much more strongly than the immersion force. Thus, the flotation force is negligible for $R < 5\text{-}10\ \mu\text{m}$, whereas the immersion force can be significant even when $R < 2\ \text{nm}$. This difference is presented in Fig. 6.6. This is an interesting result as it suggests that for the particles that are normally used for self assembly ($R < 1\ \mu\text{m}$), the capillary forces on floating particles cannot overcome the interaction forces, i.e. the energy barrier of the DLVO potential. This has far-reaching implications as considerations of novel structures such as ionic colloidal crystals normally ignore the

effect of capillary forces. This is valid for floating particles. However, when it becomes necessary to extract the structures out of the suspension, it is important to consider the capillary forces if there is a substrate involved.

Fig. 6.6 Free energy of capillary interaction, ΔQ , between two identical spherical particles of radius R separated at a center-to-center distance $L = 4R$. The full and the dashed lines correspond to the particle configurations for flotation force and immersion force respectively. [49]

For the case of uniform particles, the presence of the substrate acts in favor of ordering. This was briefly explained in the earlier section. Since similar particles are used to form the colloidal crystal, the capillary forces will always be attractive. Prior to feeling the effect of the substrate, the capillary forces are not strong enough to pull the particles into direct contact (due to presence of energy barrier). When the solvent is evaporated to the point that the colloidal crystal is affected by the substrate, the immersion forces start to act to pull the colloidal particles together. A plot of the capillary forces for a pair of 180 nm PS particles against the length of recession below the top of the particles is shown in Fig. 6.7. It can be seen that once the particles start to protrude out of the solvent, the capillary force rises to a magnitude of $\sim 10^4$ kT. This is enough to overcome the DLVO energy barrier between the particles. The scenario

can be adapted to the final packing of 3D colloidal crystal in the transition structure. The top layer of particles sees the layer below it as a substrate. When the whole colloidal crystal is in contact with the glass substrate, the top particles will start to feel the immersion capillary forces instead of the floatation capillary forces. The electrostatic double layer will collapse and there will be an immediate local increase in the ionic strength in the next layer. This increase in ionic strength is enough to collapse the double layer by strong screening effect. The effect of increasing ionic strength will cascade down the whole 3D structure until all the particles are in direct contact.

Fig. 6.7 The calculated capillary force between a pair of 180 nm polystyrene particles. The contact angle used for the calculation is 72° [60]. It is plotted against the fluid thickness (length) at infinity. As the solvent is evaporated off, the thickness will be decreasing.

If the effect of capillary forces is considered for other structures that are less packed than the FCC structure of uniform spheres, it becomes important to consider the

mechanical strength of the structures. In order to extract the structure out of the suspension, the structures must be strong enough to withstand the distortional capillary forces. The distortional forces act in favor of the formation of close-packed FCC structure. However, that may not be the case for other structures where particles can move out of the position and distort the whole structure. There is no calculation or measurement of the mechanical strength of structures like ionic colloidal crystals in the literature. Thus, it is not possible for us to predict the stability of the structures against capillary forces. Future work on the stability of the structures can help in overcoming the difficulties to achieve the structures.

Besides capillary forces, the meniscus has another important role as the dynamic boundary that confines the colloids to increase the volume fraction. In the vertical setup, it is easier to obtain highly ordered colloidal crystals due to the concave profile of the meniscus as compared to the case in sessile drop configuration. This observation can help us explore the role of the meniscus in the self assembly. In the early stage of self assembly of colloidal crystal, the meniscus boundary does not play an active role since the formation of the FCC transition structure is not affected by the boundaries. However, as the evaporation continues and the meniscus starts to enclose the colloidal crystal, the shape of the meniscus boundary becomes important. An ideal moving boundary in the self assembly is one that acts in a way that complements the directional nature of the growth process. The concave profile for the meniscus can be considered to be closer to the ideal case than the convex profile (Fig. 6.8).

Fig. 6.8 The local curvature of the meniscus in the vertical (left) and sessile drop configuration (right).

The top of the meniscus profile is the region at which the colloidal crystal is compacted. With a convex profile, there is an effective force to compress the colloidal crystal onto the substrate. This has two advantages. Firstly, it helps to overcome the electrostatic repulsion between the substrate and the colloidal crystal so that the short range Van der Waals' forces can act and adhere the colloidal crystal to the substrate. The second advantage is that in order for the capillary forces to be strong enough to act (from floatation to immersion capillary forces), the colloidal crystal must be compressed against the substrate so that the effect of the substrate can be felt.

The meniscus boundary also affects the thickness of the colloidal crystal grown. There is a dynamic equilibrium at the edge of the meniscus. The incoming evaporative solvent flux carries particles to the edge while the meniscus is receding downwards. At steady state, this will determine the amount of deposit at the edge and thus, the thickness of colloidal crystal. Simple analysis based on the balance of solvent flux and particle flux was done by Dimitrov et al. [61] and subsequently modified by Jiang et al. [9] The equation proposed by them is as follow,

$$k = \frac{\beta l \varphi}{0.605d(1 - \varphi)} \quad (44)$$

where k is the number of layers, l is the meniscus height, β is a coefficient relating the water molecule velocity to the particle velocity and is taken to be 1, d is the particle diameter, and φ is the particle volume fraction in solution.

In our experiments, some of the observations are different from what their analysis predicts. For example, it is possible to change the slope of the macroscopic meniscus boundary by adding surfactants into the suspension. As mentioned before, there are three main categories of surfactants, namely anionic, cationic and non-ionic surfactants. All the surfactant classes affect the contact angle and thus, the meniscus height. However, in order not to change the interaction between the particles which is expected to affect the coefficient β , non-ionic surfactant are used to change the conditions at the meniscus. When we increase the surfactant concentration (in turn the meniscus height, l), it is found that the thickness decreases. This can be seen from the photograph of deposited colloidal crystals in Fig. 6.9. Thicker colloidal crystals are grown from suspension with low surfactant concentration. This highlights the limitation of the equation above. The relative size of the particles with respect to the meniscus is ignored in their analysis. However, this is an oversimplification of the process, especially when combined with the mechanism of self assembly observed in our experiments. The presence of the transition structure means that prior to arrival of the particles to the true meniscus edge; the transition structure will feel the effect of confinement from the meniscus boundary. The dynamic equilibrium has to be modified to account for this confinement effect and the finite size of the transition structure. Limited knowledge of the true meniscus height prevents us from performing

a quantitative analysis of such a model. However, a qualitative explanation of the difference in dependence with the meniscus height can be given. When the meniscus height is higher and the profile of the meniscus is steeper, the confinement effect will be felt earlier by the crystallites of the transition structure before they can grow larger in size. Thus, less colloidal particles can be deposited on the same area and thinner colloidal crystals results from that. Another observation is that when the films are thick, they tend to peel off easily. This is probably due to the large stresses associated with the shrinkage of a thick film. It has also been observed by other groups that thicker colloidal crystal produces more cracks [62, 63].

Fig. 6.9 Photograph of the colloidal crystals grown with various surfactant concentration (decreasing from left to right). It can be seen that at high concentration, almost no colloidal crystals is deposited on the substrate. The thickest colloidal crystal is grown from the suspension with the lowest surfactant concentration and shows brilliant color due to the PBG effect. Higher crack density in the thick colloidal crystal also causes some peeling from the substrate.

Chapter 7: Defect Minimization in Colloidal Crystal

The presence of defects like vacancies, dislocations and drying cracks are consistently observed in colloidal crystals. These are extremely difficult to eliminate and currently limit the use of colloidal crystals as practical 3D PBG materials. The PBG is extremely sensitive to the presence of defects because they act as perturbations in the periodicity of the nanostructures and introduce defect states in the bandgap. Thus, it is necessary to minimize the defect density in colloidal crystals in order to fulfill its potential as 3D PBG materials.

Making use of the knowledge of the self assembly process gained from the in-situ structural changes, it is possible to engineer the conditions under which the deposition takes place and obtain colloidal crystals with low defect density. Firstly, a microscopic approach is examined. In this approach, we make use of the presence of the transition structure and the range of interaction to improve the quality of the colloidal crystal. Another microscopic approach to control the quality of the colloidal crystal by changing the interaction forces will also be discussed. Finally, the macroscopic effect of the meniscus boundary will be combined with the microscopic approach to identify the optimum conditions for good quality colloidal crystal.

7.1 Transition State Annealing

The transition state offers an opportunity to remove most of the defects in the colloidal crystal. In this state, the colloidal particles have a layer of solvent surrounding them while they are assembled in a FCC structure. Thus, the colloidal particles can

rearrange to anneal out defects in the transition structure due to their high mobility. They also have a larger lattice parameter affording more space for movement. On the other hand, the final colloidal crystal is made up of rigid particles mechanically locked in their position in the FCC structure and any rearrangement to remove the defects will involve a much larger distortion throughout the colloidal crystal. The energy for removing any defect is much higher in the final structure than in the transition structure. This can be seen from the schematic below. Thus, it is easier to reduce the defect density during the period at which the transition structure is stable.

Fig. 7.1 Transition structure (left) has a higher mobility due to the layer of solvent around the colloidal particles. The rearrangement of particles to remove the vacancy involves less distortion in the colloidal crystal as compared to the final dried colloidal crystal on the right.

The PBG change during the formation of the transition structures can be utilized to demonstrate the possibility of annealing to remove the defects. In this case, the experiment was done on the sessile drop configuration. During the self assembly process, the reflectance spectra were collected in an optical setup as described earlier. The reflectance changes were captured in-situ and these are indicative of the structural changes of the assembling colloidal crystal.

The result shows that there is a decrease in the defect density as the structure is held in the transition state. The reflectance spectra shown in Fig. 7.2 correspond to the period just before the final drying process when the transition structure is stable. The stability

of the transition structure is due to the continued influx of solvent for the center of the drop. This compensates for the solvent loss by evaporation at the drop edge and maintains the transition structure. A typical evolution of the reflectance spectra during this time is shown in Fig. 7.3.

Fig. 7.2 Reflectance spectra evolution during the existence of the transition structure. Notice the increasing peak intensity at a constant peak position. This indicates an improvement of the quality of the colloidal crystal. Timing starts from the initial deposition of the sessile drop of colloid suspension on a glass substrate.

Two characteristics of the evolution can be observed. Firstly, it can be seen that the peak wavelength remains constant throughout the process. This suggests that the transition structure is sustained with a constant lattice parameter. This is possible due to the solvent flow to the edge of the sessile drop. The solvent flow balances out the evaporation flux, thereby, sustaining the existence of the transition structure. The second characteristic is that it can be seen that the reflectance peak intensity is increasing with time. This is likely due to the slow decrease in the defect density of the

colloidal crystal. It is well-known that the defects of a material can be annealed out of the material by keeping the material in a state with high mobility and allowing it to equilibrate. In the case of colloidal crystal, the dried structure is rigid and the particles have no mobility to rearrange themselves to remove the defects. However, the transition structure has enough mobility for rearrangement.

Fig. 7.3 The plot of the peak wavelength and intensity against the time from the initial deposition of the colloidal suspension. There is no peak observed for the initial 15 minutes. In the period from 19 minutes to 22 minutes, there is an increase of peak intensity at constant wavelength. Finally, an abrupt change in the wavelength occurs at the end of CSA process.

The lifetime of the transition structure can be extended for the system to have sufficient time to anneal out the defects completely. This can be done by lowering the evaporation rate after it is formed. A good way of achieving this is by increasing the relative humidity of the environment. At present, the experiment is carried out in an environment of 20 % relative humidity and temperature of 50°C. This allows us to achieve drying at a reasonably fast rate. The in-situ reflectance spectroscopy of the

CSA process can help to identify the optimum time to increase the relative humidity of the environment. This will extend the lifetime of the transition structure but not decrease the efficiency of the process.

Finally, the effectiveness of the annealing process can be estimated by looking at the minimum vacancy concentration that can be achieved. Based on thermodynamics, there is an equilibrium concentration of vacancy which is determined by the vacancy formation energy. Since the transition structure is FCC which is the equilibrium structure, the minimum vacancy concentration is equal to the equilibrium concentration. For a hard sphere system, this has been calculated to be $\sim 2.4 \times 10^{-4}$ [64] which set the limit for the effectiveness of the annealing method to decrease the defect density. After looking at the possibility of making use of the transition structure, the idea of transition structure can be extended further to look at its effect on the quality of the colloidal crystal. The final transformation to the final colloidal crystal is another possible period where defects can be introduced. This is in turn intimately linked to the interaction forces between the particles.

7.2 Effect of Interaction Forces on Ordering

The interaction forces play an important part in the self assembly process as shown in the results so far. Thus, a reasonable premise is that the quality of the colloidal crystals obtained by self assembly is strongly dependent on the interaction forces between the colloidal particles. For colloidal interactions, one important parameter is the ionic strength of the suspension. The ionic strength affects the range of the electrostatic forces between the colloidal particles and in extreme cases, destabilizes the colloidal suspension. This highlights the possibility that the ionic strength can affect the quality

of the colloidal crystals significantly. As mentioned earlier, during the last stages of self assembly, an abrupt collapse of the double layer in the transition structure will occur. The relative speed of this process will determine whether the order gained during the transition state can be sustained (Fig. 7.4). If the transformation is too fast, there is a possibility of new defects nucleating in the final colloidal crystal. The thickness of the diffuse electric double layer can vary with the ionic strength of the solvent and affect the magnitude of the collapse. This is found to affect the order quality of the colloidal crystal profoundly.

Colloidal suspensions of different starting ionic strength are deposited on glass substrates. SEM images of the resulting colloidal crystals are shown in the Fig. 7.5 to Fig 7.7. It can be seen that without any salt added, the structure is less ordered and there are a lot of empty spaces between the colloid particles. This is related to the transition structure previously observed. For the low ionic strength, the final colloidal structure has significant amount of void between the particles because the initial transition structure has a larger lattice constant. The large shrinkage stresses prevent the capillary forces from packing the colloids into a truly close packed structure. In the case of intermediate ionic strength, it can be seen that better ordering of the colloidal crystal is achieved. This can be attributed to the decreased lattice constant of the transition structure in suspension of intermediate ionic strength. This suggests that the optimum condition for colloidal self assembly is with higher ionic strength of the solvent as the strong screening by the counterions reduces the electrostatic repulsion and minimal shrinkage stress will be experienced by the colloidal crystals. In this way, highly ordered colloidal crystal can be formed. However, this is not what we observe experimentally. This is due to the requirement for the stability of the colloids in

suspension. At extremely high ionic strength, colloid particles can become unstable and agglomerate into small aggregates. These aggregates are disordered and very strongly held together by the Van der Waals forces between the particles. During colloidal self assembly, capillary forces are not strong enough to break up these aggregates for rearrangement into the final FCC colloidal crystal and this can be thought as a colloidal glassy phase.

Fig. 7.4 Smaller shrinkage from the transition structure causes more stress to develop in the final colloidal crystal. This decreases the quality of the colloidal crystals grown from low ionic strength suspensions.

Fig. 7.5 SEM image (top) of colloidal crystal grown from an initial suspension without any added salt. The corresponding Fast Fourier Transform (FFT) of the image (bottom) showing poor order.

Fig. 7.6 SEM image (top) of colloidal crystal grown from an initial suspension with 1 mM ionic strength. The corresponding Fast Fourier Transform (FFT) of the image (bottom) showing good six fold order.

Fig. 7.7 SEM image (top) of colloidal crystal grown from an initial suspension with 100 mM ionic strength. A glassy structure is formed. The corresponding Fast Fourier Transform (FFT) of the image (bottom) showing extremely poor order.

7.3 Conditions for good colloidal crystal growth

In the final part of this chapter, the optimum growth conditions for high quality colloidal crystal will be summarized. Based on the understanding of the self assembly process from in-situ PBG monitoring, several factors has been identified to affect the final quality of the grown colloidal crystal. They can be categorized as microscopic factors and macroscopic ones. It is easier to understand the rationale by looking at the stages of self assembly and bringing in the relevant factors at each point. The solvent condition in the starting suspension is important to achieve good order. The colloidal particles must be able to stay dispersed in the suspension. Thus, the energy barrier in the DLVO potential cannot be eliminated and this means that either highly charged particles or low solvent ionic strength are desirable quality of the initial suspension. As the volume fraction increases during self assembly, the particles will equilibrate to a FCC transition structure. This state should be held for sufficient time in order to minimize the defect density that may be present during the initial growth. At this point, the effect of the macroscopic boundary comes into play. The substrate is desired to have the same charge as the particles in order to prevent premature adsorption of the particles. Another desirable quality is that the meniscus should be thin enough for the good coverage. This can be achieved by introducing surfactant molecules into the suspension to lower the contact angle at the meniscus. The choice of surfactant type is also important. In order to maintain control of the ionic environment in the suspension, non-ionic surfactants are preferred. In the final stages of colloidal self assembly, there is an abrupt collapse of the double layer around each particle. This process has to be controlled to prevent any new nucleation of defects in the final structure. This can be achieved by reducing the shrinkage of the double layer which is easily done by increasing the ionic strength of the suspension. Interestingly, this is against the initial

requirement for stability of the colloidal suspension which calls for low ionic strength. Thus, the optimum ionic strength for self assembly is an intermediate one. A good measure of this ionic strength can be obtained by comparing the thickness of the double layer to the particle diameter. Based on our experience, a good ratio to work with for sub-micron particles will be for a double layer thickness 10 % of the diameter of the particle. In summary, in order to grow high quality colloidal crystals, initial suspension with intermediate ionic strength can be used for deposition. The required ionic strength can be calculated by looking at the DLVO potential of the colloidal suspension. As a guideline, the added ions should result in a potential with an energy barrier of ~ 10 kT. This will give a transition structure with a smaller lattice parameter for less shrinkage and the suspension will stay stable against irreversible agglomeration.

Chapter 8: Conclusion and Future Work

So far, the model for the self assembly of colloidal particles has been described with reference to our experimental results. The key features of the model can be summarized as two stages of self assembly based on the dominant forces acting during the process. This is a useful method as it helps to identify the different conditions to consider for achieving good quality crystal growth. In the first stage, there is still ample solvent surrounding each particle and they do not feel the effect of the boundaries. The interaction forces between the particles are the dominant driving force for any ordering at this stage. From the phase diagram of colloidal suspension, FCC structure will crystallize above a critical volume fraction. Most practical applications require the colloidal crystal to be in air so the colloidal suspension is dried. The drying process initiates the self assembly process as it increases the volume fraction of the suspension. Depending on the geometry of the system, the volume fraction can be increased locally at certain regions. It is at these regions where the first colloidal crystal is formed. This phase transformation is a thermodynamic equilibrium one, thereby providing the best opportunity to reduce the defect density in the final nanostructure. An interesting finding is the appearance of a transition structure that is a manifestation of the microscopic forces in play. In the interaction potential of mono-disperse charged colloids, there is an energy barrier to prevent irreversible agglomeration of the particles. This stabilizes a FCC structure with lattice parameters larger than that of a FCC structure with particles in direct contact. This transition state can be exploited to lower the defect density as it has a higher mobility than the final structure. The experimental results support the effectiveness of the transition state as an avenue to reduce the defect density.

At the end of the first stage, the effect of the boundary will start to be felt by the colloidal crystal. In the second stage of self assembly, the meniscus starts to confine the colloidal crystal and the dominant force is the capillary force. This can affect the equilibrium colloidal crystal significantly. For good quality nanostructure, the equilibrium colloidal crystal has to maintain its order throughout the second stage of self assembly. Thus, the effect of the boundary must act in favor of the final packing of the colloidal crystal. The effect of the substrate is more subtle as compared to the meniscus. In the self assembly process, the substrate should play an indifferent role. Any prematurely adsorbed particles on the substrate can frustrate the deposition of the equilibrium colloidal crystal. A simple requirement for the substrate is for it to have the same charge as the particles. As for the meniscus boundary, it has a complicated role in the process as it is the dynamic boundary that compact the structure in the end. Its effect cannot be avoided as long as the final structure needs to be in air. Firstly, the meniscus controls the thickness of the deposited colloidal crystal. Typically, there are more defects in a thicker colloidal crystal so it is more desirable to have a smaller contact angle. The meniscus also provides the capillary force to initiate the final packing of the colloidal crystal from its transition structure. This final packing is a relatively rapid process compared to the rest of the assembly and can nucleate new defects as it is a non-equilibrium transformation. Thus, the shrinkage has to be minimized to ensure that the stresses created can be relieved during the process by cracking. This also means that macroscopic cracks cannot be avoided for high quality colloidal crystal but it can be minimized. With good control of the transformation in the second stage, it is possible to preserve the equilibrium order obtained in the first stage over a large area. Finally, this understanding of the self assembly process will

help us assess the right conditions to grow high quality 3D nanostructures without the need to go through the trial and error stage of process optimization.

A few suggestions for future work will now be proposed. Firstly, a suggestion about mono-disperse colloidal systems will be proposed. The ideal case for 3D PBG materials is to have a defect-free structure. In the case of colloidal self assembly, the most commonly observed intrinsic defects are vacancies. Based on our model of equilibrium colloidal crystal formation, it appears that vacancies cannot be totally eliminated. However, a possible solution inspired by defect gettering in semiconductors is to redistribute the vacancies in the colloidal crystal. Then, there will be a region of vacancy-free colloidal crystal which can be used for device fabrication. A way to redistribute the vacancies is to apply an electric field to the colloidal crystal in the first stage of self assembly. This field can drive the colloidal particles to fill up the vacancies as the particles are charged. As mentioned earlier, cracks are inevitable in colloidal crystals. However, they can be minimized to obtain large areas of crack-free crystal for device fabrication. This will require a theory that can predict the crack density in any structure grown by colloidal self assembly. Theories on cracking in brittle materials usually require the mechanical properties of the material to be known. In the case of colloidal crystal, this can be calculated by simulation technique but there has not been any work done on this. Thus, if calculation of the mechanical properties like elastic constant can be done, a theory of cracking in colloidal crystal can be developed and tested by experiments.

Besides mono-disperse colloidal suspension, multi-component colloidal suspension has also been found to exhibit thermodynamic equilibrium ordering. One interesting

subset of this is the ionic colloidal crystal (ICC) [65]. Two particles of opposite charges can be mixed in a suspension and they will form ordered structure controlled by the ratio of the charges and the ionic strength of the suspension. This is a powerful idea as there are many more structures other than FCC that can be obtained through this method. In particular, the Zinc Blende structure is the ionic crystal analogue to the diamond cubic structure and can exhibit a full 3D PBG. Thus, a lot of interest has been generated around this topic. Using our technique of in-situ PBG monitoring, it is also possible to examine the structural changes during the formation of ICC. It is much simpler to implement than Confocal Laser Fluorescence Microscopy used now to observe such crystals. Thus, there is a need to compute the PBG structure of various possible ICC and this can be done by making use of the MPB software. At the same time, the effect of confinement by the meniscus has to be studied to test whether the ICC formed can withstand the distortional capillary forces. In the same way that ionic crystals are brittle, ICC can be expected to be strongly affected by the capillary forces as they cannot undergo plastic deformation. Thus, the mechanical strength of the ICC can be calculated to predict their stability against capillary forces. This can help realize the potential of ICC to achieve full 3D PBG with a one step self assembly process.

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