Soft colloids in confinements

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SOFT COLLOIDS IN CONFINEMENTS

KRONGTUM SANKAEWTONG

School of Chemical and Biomedical Engineering

2020

SOFT COLLOIDS IN CONFINEMENTS

KRONGTUM SANKAEWTONG

School of Chemical and Biomedical Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

2020

Statement of Originality

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Chapter 2 is published as [Krongtum Sankaewtong, Qun-li Lei and Ran Ni, *Self-assembled multi-layer simple cubic photonic crystals of oppositely charged colloids in confinement*, *Soft Matter*, **15**, 3104-3110 \(2019\). DOI: 10.1039/C9SM00018F.](#)

The contributions of the co-authors are as follows:

- Asst Prof Ni Ran provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Qun-li Le and Asst Prof Ni Ran.
- I co-designed the study with Asst Prof Ni Ran and Dr Qun-li Le and performed all the simulations at the School of Chemical and Biomedical Engineering. I also analyzed the data.
- All simulations, including coding of the original program, was conducted by me to study the phase behaviour and calculate the system free energies.
- Dr Qun-li Le provided guidelines on calculation of photonic property of the observed structures.

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“Everything we call real is made of things that cannot be regarded as real.”

—Bohr , Niels

To my dear family

Abstract

Colloids are ubiquitous in nature, e.g. dust, milk or blood and also exist as daily life products, e.g. paints, jelly or whipped cream. Thus, better understanding of behaviours of colloidal systems can draw paths to advancement in technologies and innovation. By confining colloidal dispersions, the systems exhibit richer phase behaviours compared to their three-dimensional bulk counterparts. For example, in the simplest model of hard spheres system, the confinement induces a phase transition **between** triangular($\triangle$) and square($\square$) symmetries with a sequence of $\dots n\triangle \rightarrow (n+1)\square \rightarrow (n+1)\triangle \dots$, where n is the number of crystal layers, which is a function of confinement height out of the FCC phase of the bulk system.

Throughout this thesis, we study soft colloidal systems in topographical confinement. In chapter 1, we provide general backgrounds of colloidal systems and the simulation method we applied, i.e. Monte Carlo simulation method. In chapter 2, the system of confined oppositely charged colloids are studied in their phase behaviour. The oppositely charged colloids have been reported to form FCC and BCC phases in bulk systems. By confining the suspension between two parallel hard walls, we demonstrated a novel phase of NaCl-like (Simple Cubic structure) open crystals which can be stabilized up to several layers. The maximum number of layer of the phase is an inverse function with the inverse screening length. Moreover, at finite low temperature, the multi-layer NaCl-like crystals can be stabilized against the most energetically favored close-packed crystals by large vibrational entropy. We found up to 4-layer NaCl-like crystal as a stable phase in this confined system, in the range of parameters studied. The photonic properties calculation shows that the inverse 4-layer NaCl-like crystal can already reproduce the large photonic band gaps of the bulk simple cubic crystal, which open at low frequency range with low dielectric contrast. This lights up new possibilities of using confined colloidal systems to fabricate open crystalline materials with novel photonic properties.

In chapter 3, the nucleation of the novel multi-layer simple cubic crystal we found in confined oppositely charged colloidal systems in chapter 2 is studied. By implementing umbrella sampling Monte Carlo method, we calculated Gibbs free-energy barriers in supersaturation region $0.33 \leq \beta|\Delta\mu| \leq 0.47$. We also fit the numerical results with the classical nucleation theory assuming spherical and cylindrical shapes of the nucleus. The fitting with assuming cylindrical configuration shows better alignment which is caused by the surface term differences of both shapes wherein the cylindrical surface term the confinement parameter is included while the spherical one is only a function of cluster size and its density.

Then, we switch our attention to the system of like-charge repulsive system in chapter 4. By comparing the simulation results and experimental data, we found FCC-BCC reentrance which is different from the confined hard-sphere system in the regime where the BCC lattice is the stable phase in the bulk system. The numerical results show that this reentrance is governed by the entropy and can be stacked up to 14 layers whereat the FCC phase becomes rare. This can pave a novel pathway of bottom-up approach for fabricating micro- or macroscale colloidal crystal films with highly complicated nanostructures.

Last but not least in chapter 5, we exploit the confinement to eliminate vacancies formed in colloidal crystals of magnetic dipoles systems confined between a flat wall and a curved wall. The illustration of the trajectory of a single vacancy shows that the vacancies travel through the phase space and merge with the perturbed region induced by the curved wall at last. The traveling time to the curved wall is system size dependent with no correlation with the initial position of the vacancy in the crystal. We found that at the curved wall with radius of the curvature of 4.5σ , the vacancy can diffuse fastest. For the two-vacancies case, the vacancies bind to each other and diffuse towards the curved wall.

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Symbols and Acronyms

Symbols

a	lattice constant
c	speed of light
F	Helmholtz free energy
$g(r)$	radial distribution function
G	Gibbs free energy
h	confinement height
H	enthalpy
$\mathbf{H}$	magnetic field
k_B	Boltzmann's constant
L	length of a side of a simulation box
M	total number of Monte Carlo samples
N	number of particles
P	pressure
$P(o)$	robability density of finding a system in configuration o
P_{NVT}	probability density for canonical ensemble
P_{NPT}	probability density for isobaric-isothermal ensemble
$p_{acc}(A \rightarrow B)$	acceptance probability of moving from configuration A to configuration B
$Q(N, V, T)$	canonical partition function
$Q(N, P, T)$	isothermal-isobaric partition function
r_c	cut-off radius of a potential
r_i	Cartesian coordinate of particle i
r_{ij}	center-to-center distance between particle i and particle j
R	radius of a nucleus
s_i	scaled coordinate of particle i
S	the entropy of the system

$t(A \rightarrow B)$	probability of generating configuration B starting from configuration A
t	time
T	temperature
U	internal energy of the system
$U(o)$	potential energy of configuration o
V	volumn
$W(A \rightarrow B)$	transition probability from configuration A to configuration B
Ze	charge of a particle
β	reciprocal temperture ($1/k_B T$)
ϵ_s	the dielectric constant of the solvent
η	packing fraction
γ	interfacial free energy
Γ	coupling parameter
κ	inverse Debye screening length
λ	spring constant
λ_B	Bjerrum length
μ	chemical potential
ω	frequency
ρ	number density
σ	diameter of a paticle
$\langle \dots \rangle$	ensemble average
$\langle \dots \rangle_{sub}$	ensemble average under condition indicated by <i>sub</i>
∇f	the gradient vector
$\bullet$	vector dot product
$\times$	vector corss product
X^T	transpose of matrix X
$/$	division
$\sqrt{}$	square root

Acronyms

DLVO	Derjaguin-Landau-Verwey-Overbeek
------	----------------------------------

BCC	Body-Centered Cubic
FCC	Face-Centered Cubic
LEDs	Light-Emitting Diodes
CNT	Classical Nucleation Theory
MC	Monte Carlo
NPT	Isobaric-Isothermal Ensemble
NVT	Canonical Ensemble
EOS	Equation of State
US	Umbrella Sampling
HCP	Hexagonal Closest Packed
MSD	Mean Square Displacement

Chapter 1

Introduction

Colloids

Colloids are a mixture where small particles are suspended in a fluid phase which acting as the dispersing medium. Their size range is typically between ~ 10 nm to several micrometers. Colloids are actually common in everyday life with some examples including whipped cream, mayonnaise, milk, jelly, colored glass and paper. Since we involve the colloids in our daily life, colloidal suspensions are very important technologically, i.e. the character of the mixture that allows solid particle to flow like a fluid, they have been used in various applications from inks, coatings and critical diagnostic tests. Thus, the better understanding of the behaviour of colloidal systems can lead to advancements in producing these products. Furthermore, colloidal systems behave similarly to atomic and molecular systems and can serve as good model systems for condensed matter physics. At a given temperature, the colloidal particles move in a random motion i.e. Brownian motion [1] occurs due to the collision between the particles with the fast-moving molecules in the fluid, the particles can explore phase space and self-assemble similarly to atomic and molecular systems. Besides, the colloidal particles are several orders of magnitude larger than atoms or molecules, and they move much slower, which makes the system possible to be tracked in its motion in real time using an optical microscopy enabling studies of the dynamics of physical processes e.g. nucleation, melting, (Ed)mixing, freezing, glass transition, gelation either spontaneous or externally

driven by templates, gravity or electric field which are strenuous to investigate for atomic or molecular systems.

In addition, the tunability of the interactions between colloidal particles inaugurates the possibility of crafting functional material with designed properties. By nature, colloids are charged particles since their surfaces always absorb ions and release some ions, in exchange, to the solvent. These charged stabilized colloids are mainly governed by a Yukawa-like pair interaction [2] for which the pair interaction can be described by the Derjaguin-Landau-Verwey-Overbeek (DLVO) pair interaction involving the linear Poisson-Boltzmann theory [3]. The solvent ions screen the bare Coulomb interaction between charged colloids. By changing the concentration of substances in the solvent, one can tune the strength of interaction between the particles. When the concentration of ions is low, the electrostatic repulsion dominates the phase behaviour and leads the aggregation to a body-centered cubic (bcc) crystal at high density. Adding salt into the solution, the interaction is, then, tuned to a hard-sphere like repulsion which leads the formation of the face-centered cubic (fcc) [4]. Furthermore, we can also tune the interaction by modifying the the shape of particle, e.g. introducing patches on the surface of the particle can lead to anisotropic interactions or presenting the non-adsorbing polymer can result in effective depletion attractions [5,6].

Colloidal particles can assemble to numerous structures and phases. Fabricated materials from colloids self-assembly are called "nanomaterials". Colloidal crystals differently exhibit physical properties from atomic or molecular crystal. The energy densities of the colloidal system are relatively lower compared to the atomic systems since the length scale cooperated in colloidal system is much longer than that of atomic and molecular distances ($< \text{nm}$) while the interaction energies among the particles are commensurate to the atomic systems [7]. Thus, the colloidal crystals are rather very *soft* compared to the atomic systems, soft in terms of lower elastic or shear moduli up to ten to twelve orders of magnitude.

Colloidal crystals in which their structure are periodically repeated in space on the scale of tens to hundreds of nanometres making these materials exquisitely befit for the manipulation of (visible) light [8]. Thus, colloidal crystals with their lattice spacing comparable to the wavelength of light are perfect candidates for the crafting of photonic bandgap materials [9,10] with potential applications in solar cells, sensors, highly efficient light-emitting diodes (LEDs) and optical computing

chips. The potential applications of the spontaneous self-assembly of colloids open the cheaper path for crafting nanostructures which require not only the availability to manipulate the properties of the crystals but also a better understanding of the relationship between the building blocks, inter-particle interaction and the structures. Crystallization from a metastable liquid can be separated into two categories: *homogeneous* and *heterogeneous* nucleations. The homogeneous nucleation can be described by the classical nucleation theory (CNT) [11] which involves the formation of a crystal nuclei of a critical size cluster in the liquid phase. In contrast, heterogeneous nucleation arises by a heterogeneity on the system, e.g., impurities or walls.

Since the difference in particle shapes and interactions gives rise to different packing entropy, S , and interaction energy, U , in minimizing the free energy of a system, $F = U - TS$, where T is temperature, thus, resulting in different phases at equilibrium. For the simplest case of hard spheres, the phase behaviour is purely governed by the entropy since the interaction of the system only induced by excluded volume effects, i.e., hard-core interaction $U = 0$. The system tends to form the fcc phase in 3D due to its efficiency of utilizing the space that is the phase having greater free-volume entropy [12]. Crystals in lower dimensions have more long-wavelength fluctuations since they have fewer neighbours to bind each particle on its lattice site. Thus, crystals are too soft to be stable in 1D unless there are long-range interactions involved. For the 2D case, the crystals are very soft with only quasi-long-range translational order and long-range orientational order.

Introducing confinement to a colloidal system can alter the entire behaviour of the system. Confinements can be, generally, classified into two classes: topographical confinements and energetic confinements. The first type of confinements can be realized as the geometrical restriction to a system such as putting a colloidal system into a slit-pores or between walls/wedges or in real world system such as cells, while the second type of confinement is the contribution from potential fields, e.g. gravity, or by the shape of the interparticle-interaction itself. In this thesis, we only concern on the first type of confinement.

The systems under confinement exhibit dramatically different behaviour from the bulk. In the case of the hard-sphere system, the bulk phase diagram is purely dictated by the volume fraction η . The first order fluid-to-crystal transition is controlled by the entropy of the system, i.e. entropy-driven phase transition [13]. The

lower in the configurational entropy of the entire system owing to the formation of a crystal phase is overcompensated by an increase in the entropy from the larger free volume in a crystal lattice. Thus, results in increasing of the net entropy. The fluid freezes to form a crystal, face-centered-cubic (FCC), at $\eta_f \approx 0.494$. On the other hand, the FCC crystal starts to melt at $\eta_m \approx 0.545$ and the system of the volume fraction between η_f and η_m exhibits the coexistence between a fluid and a fcc crystal [14]. Confining the system with hard walls can lead to a phenomenon called capillary freezing which the whole fluid in the slit freezes at thermodynamic state points where the bulk is still a fluid [15]. The opposite phenomenon called capillary melting can also occur [16]. These behaviours are strongly influenced by the plate separation. In the study, the coexisting solid phase consists of crystalline layers with either triangular or square symmetry. By increasing the plate separation, the well-known sequence of $\dots n\Delta \rightarrow (n+1)\square \rightarrow (n+1)\Delta \dots$, where n is the number of crystal layers, is observed. The hard-sphere system under quasi-2D confinement can also form triangular, square and buckled thin-film crystals [17].

By introducing charges into the system, the particles become *softer* i.e. charged hard spheres, one can mimic the behaviour of ionic systems. The phase behaviour of this system can be understood on the basis of the DLVO screened Coulomb potentials in which the screening is due to the presence of coions and counterions in the solvent. The theory combines the effect of the van der Waals attraction and the electrostatic repulsion due to the so-called double layer of counterions. When two particles come closer, the electrostatic repulsion increases as the interference between their double layers increases. Whereas, the Van der Waals attraction increases as they get closer. The long-ranged Coulomb interactions can introduce more phases from the hard-sphere system e.g. CuAu structure which has body-centered cubic (BCC) symmetry [18].

In this thesis, we mainly focus on studying systems in topographical confinement. Detailed studies for bulk hard sphere [19], bulk oppositely charged colloids [18] and confined hard sphere [17] were performed but the one for the confined oppositely charged particles is missing. Furthermore, the confined oppositely charged system has potential to self-assemble into a diverse array of structures that are not observed in their bulk system. Thus, in Chapter 2, we close this gap and exhibit the equilibrium phase behaviour of oppositely charged particles confined between two hard flat walls. Then in Chapter 3, we further investigate the nucleation of

the open crystalline structure we found in Chapter 2 by using umbrella sampling simulation. In Chapter 4, we turn our attention to study phase behaviours both experimentally and by simulation of the purely repulsive Yukawa system confined in wedge. Lastly in Chapter 5 motivated by the fact that vacancies in a crystal phase are interacting, we study the effect of the curved hard wall that is confining dipolar systems on the behaviour of vacancies mobility.

Monte Carlo simulations

In this thesis, we perform computer simulations to study the equilibrium phase behaviour of the soft colloidal systems. The main simulation method employed is the Monte Carlo (MC) simulations. To determine the equilibrium properties of a colloidal system, Monte Carlo simulations are employed to sampling the phase space according to a Boltzmann distribution. The following paragraphs are denoted to give a brief explanation for the method.

Consider a system of N interacting particles in a volume V at temperature T . The probability of the system to be in a state with particle position $\mathbf{r}^N$ proportional to the Boltzmann weight with respect to the potential energy U of the system:

$$P_{NVT}(\mathbf{r}^N) \propto \exp[-\beta U(\mathbf{r}^N)] \quad (1.1)$$

where $\beta = 1/k_B T$ and k_B is the Boltzmann constant. The mathematical expression of a quantity A of the system is the weighted average of A over all possible states:

$$\langle A \rangle_{NVT} = \frac{\int d\mathbf{r}^N A(\mathbf{r}^N) \exp[-\beta U(\mathbf{r}^N)]}{\int d\mathbf{r}^N \exp[-\beta U(\mathbf{r}^N)]} \quad (1.2)$$

where the partition function of this system is given by

$$Q(N, V, T) \equiv C \int d\mathbf{r}^N P_{NVT}(\mathbf{r}^N) \quad (1.3)$$

where C is a constant.

The value of $\langle A \rangle$ in Eq.1.2 can be conventionally determined by using numerical integration techniques, e.g. quadrature. Nonetheless, these techniques measure the value of the integrand at a **predetermined** set of points which the evaluation will become futile in high dimensional space since the number of gridpoints is tremendous. For example, in a 3-dimensional system with 100 particles, the total number of coordinate is 300. If one only use a very rough 6 points per axis in the configurational space, the total number of points that will be evaluated is 6^{300} which sounds hopeless. Furthermore, in these conventional techniques, many gridpoints are located in regions where the integrand, Boltzmann factor, vanishes, e.g. for a typical liquid which most of configurations $\mathbf{r}^N$ are zero and only exceptionally limited parts of the phase space contribute nonzero value to $Q(N, V, T)$.

The Metropolis method

As stated above that using the conventional methods is simply out of the question. We now have to consider a better way to determine the equilibrium average properties of a system. This can be done by the Metropolis algorithm [20] where the Monte Carlo simulation samples simply the most relevant states of the system. The basic idea is points in configuration space are generated according to the desired probability, in the region where the integrand is nonzero. By generating configuration $\mathbf{r}_i^N$ in such a way that the propability of generating is proportional to a Boltzmann distribution $\exp[-\beta U(\mathbf{r}_i^N)]$, the average in Eq.1.2 becomes

$$\langle A \rangle_{NVT} = \lim_{M \rightarrow \infty} \frac{1}{M} \sum_{i=1}^M A(\mathbf{r}_i^N) \quad (1.4)$$

To generate configurations according to the desired distribution $P(\mathbf{r}^N)$, we can create a random walk in the phase space by sampling it with the ensemble distribution. The Metropolis Monte Carlo algorithm uses a random walk in the phase space in which the system is firstly generated in a configuration $\mathbf{r}_A^N$. This configuration couples with the nonzero Boltzmann weight $\exp[-\beta U(A)]$. Next, a new random trial configuration $\mathbf{r}_B^N$ is generated by randomly picking a particle and adding a small

random displacement to its coordinates. This causes a change in the Boltzmann weight to $\exp[-\beta U(B)]$. Now, we have to decide whether this new configuration is accepted or rejected by following the **Metropolis acceptance criterion**. This scheme is constructed by considering that if $M \rightarrow \infty$, the Monte Carlo simulations are carried out for an enormous number, all configurations can be visited. Furthermore in equilibrium, the average number of accepted trial moves from state A to state B is exactly equal to the number of accepted trial moves from state B to state A . This is called detailed-balance condition. The probabilities of propagating from the initial configuration A to the new configuration B is provided by the transition probability $W(A \rightarrow B)$. The detailed-balance condition can be, then, written as

$$P(A)W(A \rightarrow B) = P(B)W(B \rightarrow A) \quad (1.5)$$

The transition probability can be written down as the product of the probability of performing a trial move from A to B by $t(A \rightarrow B)$ with the acceptance probability of the trial move $p_{acc}(A \rightarrow B)$:

$$W(A \rightarrow B) = t(A \rightarrow B) \times p_{acc}(A \rightarrow B) \quad (1.6)$$

With this relationship, the condition in Eq.1.5 becomes:

$$P(A)t(A \rightarrow B)p_{acc}(A \rightarrow B) = P(B)t(B \rightarrow A)p_{acc}(B \rightarrow A) \quad (1.7)$$

In the Metropolis scheme, the t is chosen to be symmetric ($t(A \rightarrow B) = t(B \rightarrow A)$).

Thus, the Eq.1.7 can lead to

$$\frac{p_{acc}(A \rightarrow B)}{p_{acc}(B \rightarrow A)} = \frac{P(B)}{P(A)} = \exp[-\beta(U(B) - U(A))] \quad (1.8)$$

Obviously, the probability $p_{acc}(A \rightarrow B)$ cannot exceed 1. Thus, if we generate a trial move from state A to state B , with $U(B) > U(A)$, this trial move shall be accepted due to Eq.1.8 with probability

$$p_{acc}(A \rightarrow B) = \exp[-\beta(U(B) - U(A))] < 1 \quad (1.9)$$

And we can write down the rule for accepting a trial move as

$$p_{acc}(A \rightarrow B) = \min(1, \exp[-\beta(U(B) - U(A))]) \quad (1.10)$$

This can be interpreted as once the new configuration has lower in energy, the propagation of the markov chain will always be toward that new configuration.

Isobaric-Isothermal Ensemble (NPT)

Now we extend the expression in Eq.1.10 for constant pressure Monte Carlo simulations. The partition function in Eq.1.3 describes a system with N particles, in a volume V and at temperature T . If the system is contained in a cubic box $V = L^3$, we can represent the coordinate of each particle as:

$$\mathbf{r}_i = L\mathbf{s}_i \quad i = 1, \dots, N \quad (1.11)$$

where s_i is the fractional coordinate of particle i , $s_i \in [0, 1]$. The partition function in Eq.1.3 can be, then, rewritten as

$$Q(N, V, T) = CV^N \int d\mathbf{s}^N P(\mathbf{s}^N) \quad (1.12)$$

We then couple this system with an ideal gas reservoir, with the total Volume V_o and total number of particle N_o . The partition function of this coupled system is, then, the product of the two subsystems

$$Q(N, N_o, V, V_o, T) = C_1(V_o - V)^{N_o - N} \int d\mathbf{s}^{N_o - N} P_o(\mathbf{s}^{N_o - N}) \times C_2 V^N \int d\mathbf{s}^N P(\mathbf{s}^N) \quad (1.13)$$

In the first integral, $P_o(\mathbf{s}^{N_o-N})$ is zero since we assume the particles in this region are noninteracting. Thus, the first integral yields 1. The Eq.1.13 becomes

$$Q(N, N_o, V, V_o, T) = K(V_o - V)^{N_o-N} V^N \int d\mathbf{s}^N P(\mathbf{s}^N) \quad (1.14)$$

where the constant $K = C_1 \times C_2$. To get the partition function for a constant pressure P system, we have to integrate the Eq.1.14 over the volumes

$$Q(N, N_o, V_o, T) = \int dV K(V_o - V)^{N_o-N} V^N \int d\mathbf{s}^N P(\mathbf{s}^N) \quad (1.15)$$

If the size of the reservoir is infinitely large, $V_o \rightarrow \infty$ and $N_o \rightarrow \infty$. This leads $(N_o - N)/V_o \rightarrow \rho$ and since the reservoir contains an ideal gas, $\rho = \beta P$. The volume different term in the first integral of Eq.1.15 can be written as

$$\begin{aligned} (V_o - V)^{N_o-N} &= V_o^{N_o-N} \left(1 - \frac{V}{V_o}\right)^{N_o-N} \\ &= V_o^{N_o-N} \exp\left[-(N_o - N) \frac{V}{V_o}\right] = V_o^{N_o-N} \exp[-\rho V] \\ (V_o - V)^{N_o-N} &= V_o^{N_o-N} \exp[-\beta P V] \end{aligned} \quad (1.16)$$

Then, we arrive

$$Q(N, P, T) = K \int dV \exp[-\beta P V] V^N \int d\mathbf{s}^N P(\mathbf{s}^N) \quad (1.17)$$

Again, this partition function is constructed based on the assumption that the box shape is undeformable, cubic box. The probability of the system to be in a state with particle position $\mathbf{s}^N$ and volume V , in the same manner as Eq.1.1, reads

$$P_{NPT}(V, \mathbf{s}^N) \propto V^N \exp[-\beta P V] \exp[-\beta U(\mathbf{s}^N)] \quad (1.18)$$

The ensemble the average of a quantity A is, then, given by

$$\langle A \rangle_{NPT} = \frac{\int dV \int d\mathbf{r}^N A(\mathbf{r}^N) \exp[-\beta(U(\mathbf{r}^N) + PV)]}{\int dV \int d\mathbf{r}^N \exp[-\beta(U(\mathbf{r}^N) + PV)]} \quad (1.19)$$

Now, we can determine the acceptance rule of the NPT Ensemble. If we change the volume of the system, as we have shown in Eq.1.8, the acceptance ratio can be written as

$$\begin{aligned} \frac{p_{acc}(A \rightarrow B)}{p_{acc}(B \rightarrow A)} &= \frac{P(B)}{P(A)} = \frac{V_B^N \exp[-\beta PV_B] \exp[-\beta U_B(\mathbf{s}^N; L_B)]}{V_A^N \exp[-\beta PV_A] \exp[-\beta U_A(\mathbf{s}^N; L_A)]} \\ &= \left(\frac{V_B}{V_A}\right)^N \exp[-\beta P(V_B - V_A)] \exp[-\beta[U(B) - U(A)]] \\ &= \exp \left[-\beta \left(P(V_B - V_A) + [U(B) - U(A)] - N\beta^{-1} \ln(V_B/V_A) \right) \right] \end{aligned} \quad (1.20)$$

In the case of confined systems, one direction of the simulation box is fixed, denoted by h , and the other sides can be independently varied. The volume can be then written as $V = L^2 h$. The partition function in Eq.1.17 can be reviewed to

$$Q(N, P, T) = K \int dL_x dL_y (L_x L_y h)^{N+0.5} \exp[-\beta P L_x L_y h] \int d\mathbf{s}^N P(\mathbf{s}^N) \quad (1.21)$$

The acceptance rule for the trial move from A to B when the volume is changed becomes

$$\begin{aligned} p_{acc}(A \rightarrow B) &= \min(1, \exp \left[-\beta \left(P(V_B - V_A) \right. \right. \\ &\quad \left. \left. + [U(B) - U(A)] - (N + 0.5)\beta^{-1} \ln(V_B/V_A) \right) \right]) \end{aligned} \quad (1.22)$$

Numerical implementation

All numerical results presented in this thesis are performed using in-house C++ based codes run on Intel(R) Xeon(R) CPU E52680 0 @ 2.70GHz. The C++ programmes are based on algorithms described in Frenkel and Smit handbook [21]. To speed up the simulation, we combined the algorithms with a cell list [22]. The general workflow of the Monte Carlo simulation for a system is described below:

1. Initialize the configuration, i.e. put particles on desired position; at random for the fluid case and on lattice sites for a crystal.
2. Initialize the cell list of the system by storing the list of particles in a cell.
3. Select a particle at random and calculate the energy of the present configuration
4. Give the particle random displacement and determine the energy of the proposed configuration.
5. Accept or reject the move based on Eq.1.22 and update the new position of the moving particle.
6. Repeat step 3 to 5.

It is good practice to always calculate the total energy of the system and compare with the sum of the initial energy and all energy differences of all accepted moves as these two quantities should be equal. This step is very useful to make sure the convergence of the simulation.

Chapter 2

Self-assembled multi-layer simple cubic photonic crystals of oppositely charged colloids in confinement

Introduction

One of the major goals in colloidal self-assembly is to devise new colloidal systems to self-assemble into low-density open crystalline structures [23–29], which are partially due to their promising applications in photonics [30], catalysis, porous media [31] and the special response to mechanical stress [32–34]. However, dated back to Maxwell, it has been proven that to maintain the mechanical stability, the coordination number of particles connected by central force bonds in periodic lattices must be larger than $2d$ in d dimensions [35]. Therefore, available methods for fabricating open colloidal crystals typically involve patterning the surface of colloidal particle forming anisotropic patchy particles with directional interactions [26,27,29,36–41]. It was also found that the vibrational entropy in the crystal formed by patchy particles stabilizes the low-density open crystal against the close-packed crystalline structures with the same energy [42,43]. However, making high quality monodisperse patchy colloids with well defined patches, which can self-assemble into open crystals, has been challenging in experiments [26,38,44–48].

In past decades, a significant amount of scientific attention has been devoted into the self-assembly of colloidal systems in confinement, which has become a

general way of tuning colloidal self-assembly [17, 49–61]. However, most of colloidal crystals found in confinement are close-packed. In this chapter by using computer simulation, we investigate the self-assembly of oppositely charged colloidal hard spheres confined between two parallel hard walls. Compared to the self-assembly of oppositely charged colloids in 3D systems [18, 62], we find the existence of stable multilayer NaCl-like (simple cubic) crystals, of which the square plane is parallel to the confining walls. The maximal number of layers for stable NaCl-like crystal at the ground state increases with decreasing the inverse screening length, and the vibrational entropy at finite low temperature also helps to stabilize the open multi-layer NaCl-like crystal against the energetically most favoured close-packed crystals.

Methodology

Model

We consider a system of N colloidal spheres of a diameter σ confined between two parallel hard walls in z direction, half of which carry a positive charge Ze , and the other half a negative charge $-Ze$. The wall-wall separation is h , as shown in Figure 2.1a. We employ the Derjaguin-Landau-Verwey-Overbeek screened Coulomb pair potential [63] to model the interaction between charged colloids i and j

$$\frac{U(r_{ij})}{k_B T} = \begin{cases} \pm \frac{Z^2}{(1+\kappa\sigma/2)^2} \frac{\lambda_B}{\sigma} \frac{e^{-\kappa(r-\sigma)}}{r/\sigma} & r \geq \sigma \\ \infty & r < \sigma \end{cases} \quad (2.1)$$

where r_{ij} is the center-to-center distance between two particles, and $\lambda_B = e^2/\epsilon_s k_B T$ is the Bjerrum length with ϵ_s the dielectric constant of the solvent. k_B and T are the Boltzmann constant and the temperature of the solvent, respectively. $\kappa = \sqrt{8\pi\lambda_B\rho_{salt}}$ is the inverse Debye screening length with ρ_{salt} the salt concentration. As mentioned in Chapter 1 that the DLVO theory describes the interparticle interaction between charged colloids in aqueous dispersions by combining the effects of van der Waals and electrostatic forces. Here we focus only on systems with

FIGURE 2.1: (a) Illustration of oppositely charged particles (red or blue spheres) with diameter σ confined between parallel hard walls with separation h . (b-d) Unit cells of ground states: NaCl (b), CsCl (c) and CuAu (d) crystals of the confined systems, where the shadow plane is parallel to the confining walls.

$\kappa \geq 3\sigma^{-1}$, in which the pair potential in Eq.2.1 was shown being a good approximation for modelling the screened Coulomb interaction in the system, and the multi-body effect is negligible [64]. We define the packing fraction of the system as $\eta = \pi\sigma^3 N / (6Ah)$ where A is the area of the system in $x - y$ plane, and $T^* = (1 + \kappa\sigma)^2 \sigma / Z^2 \lambda_B$ is defined as the reduced temperature, i.e., the inverse of the contact value of the potential in Eq.2.1. We assume that the confining walls are neutral and the interaction between particle i and the confining walls is dominated by the excluded volume effect

$$U_{wall-fluid} = \begin{cases} 0 & r_i \geq \sigma/2 \\ \infty & r_i < \sigma/2 \end{cases} \quad (2.2)$$

where r_i is the distance of the center of mass of particle i to the nearest wall in z direction.

Free energy calculation

Fluid phase

We employ standard *NPT* Monte Carlo simulations to obtain the equation of state (EOS) for the fluid phase, and we determine the free energy by integrating the EOS from the reference density ρ_0 to ρ :

$$\frac{F(\rho)}{N} = \frac{F(\rho_0)}{N} + \int_{\rho_0}^{\rho} \frac{P(\rho')}{\rho'^2} d\rho' \quad (2.3)$$

where $F(\rho_0)/N = \mu(\rho_0) - P(\rho_0)/\rho_0$ is Helmholtz free energy per particle at density ρ_0 , and the chemical potential $\mu(\rho_0)$ is determined by the Widom's insertion method [21].

Crystal phases in confinement

For calculating the free energy of a crystal, we use the Einstein integration method [65]. The Helmholtz free energy F of a crystal confined between two parallel walls is

$$\begin{aligned} F(N, V, T) &= F_{Einst}(N, V, T) \\ &- \int_0^{\lambda_{max}} d\lambda \left\langle \frac{\partial U_{Einst}(\lambda)}{\partial \lambda} \right\rangle_{\gamma_{max}, 1/T_{max}^*} \\ &+ \int_0^{1/T^*} d(1/T^*) \left\langle \frac{\partial \sum_{i \neq j} U(r_{ij})}{\partial (1/T^*)} \right\rangle_{\gamma_{max}, \lambda_{max}} \\ &+ \int_0^{\gamma_{max}} d\gamma \left\langle \frac{\partial [\sum_{i \neq j} \varphi(i, j) + \sum_i \psi(i)]}{\partial \gamma} \right\rangle_{1/T^*=0, \lambda_{max}} \end{aligned} \quad (2.4)$$

where F_{Einst} is the free energy of the ideal Einstein crystal. $\varphi(i, j)$ and $\psi(i)$ are the softness potentials between particle i and j and particle i with the nearest wall, respectively:

$$\frac{\varphi(i, j)}{k_B T} = \begin{cases} \gamma[1 - A(1 + \zeta(i, j))] & \zeta(i, j) < 0 \\ 0 & otherwise \end{cases} \quad (2.5)$$

and

$$\frac{\psi(i)}{k_B T} = \begin{cases} \gamma[1 - A(1 + \zeta(i))] & \zeta(i) < 0 \\ 0 & otherwise \end{cases} \quad (2.6)$$

where $\zeta(i, j)$ and $\zeta(i)$ are the surface distances between particle i and j and between particle i and its nearest wall, respectively, and they are negative when overlapped. γ is the integration parameter with $A = 0.9$ [66]. Here we choose to use $\gamma_{max} = 150$ to guarantee the hardcore interaction is reproduced at γ_{max} . $U_{Einst}(\lambda)$ is a harmonic potential used to fix the particles onto a perfect crystal lattice:

$$U_{Einst}(\lambda) = \lambda \sum_i (\mathbf{r}_i - \mathbf{r}_{i,0})^2 / \sigma^2 \quad (2.7)$$

where $\mathbf{r}_i$ and $\mathbf{r}_{i,0}$ are the position of particle i and its corresponding position in a perfect lattice, respectively. λ is the integration parameter, and we choose $\lambda_{max} = 2000$. At $h/\sigma = 1$, the crystal is exactly in 2D, and the free energy for the ideal Einstein crystal in 2D reads [67]

$$\frac{F_{Einst}(N, V, T)}{N k_B T} = -\frac{N-1}{N} \ln \left(\frac{\pi}{\lambda_{max}} \right) - \frac{\ln A \sigma^2}{N} \quad (2.8)$$

For $h\sigma > 1$, the reference ideal Einstein crystal is in 3D, of which the free energy is [68]

$$\frac{F_{Einst}(N, V, T)}{N k_B T} = -\frac{3(N-1)}{2N} \ln \left(\frac{\pi}{\lambda_{max}} \right) + \frac{\ln \rho \sigma^3}{N} - \frac{3 \ln N}{2N} \quad (2.9)$$

For calculating the integrations in Eq.2.4, we implement the 20-points Gaussian Quadrature integration method. We have ensured that error in the calculated free energy is smaller than $0.01k_B T$ per particle.

FIGURE 2.2: The common tangent procedure performs on the plot of F/V - density of the two-layer NaCl, two-layer CsCl and three-layers CsCl crystals confined between walls with the separation between the walls $h = 2.5\sigma$ at $T^* = 0.1$ with $\kappa = 6$. The slope of dash lines can be referred as the chemical potential of each phase. The red lines are the common tangents between the solid phases and the dilute vapour. At low density, the slope of the two-layer NaCl phase is lower than that of the two-layer CsCl which shows that the two-layer NaCl is more stable. We further investigate for the high density regime which the height $h = 2.5\sigma$ can facilitate the three-layers CsCl. After we map the common tangent between two-layer NaCl and the three-layers CsCl crystals, we obtained the phase boundary between the two phases at $\eta_{nacl} = 0.4138$ and $\eta_{CsCl} = 0.6072$. This common tangent illustration also shows a case that the two-layer CsCl crystal is a metastable phase since its free energy curve locates above the common tangent of two-layer NaCl and the three-layers CsCl crystals. The inset figure shows the common tangent line of the phases with the ideal gas at zero density.

To determine phase boundaries, we implement the common tangent construction

for both solid and fluid phases. However at low T^* , the strong inter-particle interaction induces the condensed phase in the fluid phase which coexists with dilute gas phase. This prevents us from comparing the free energy of the fluid phase with candidate solid phases since the Widom's method fails. Thus, for each candidate solid phase at low T^* regime, we compare the free energy with the dilute gas ($P \rightarrow 0$) and determine the coexisting packing fraction of the solid phase with the dilute vapour at zero pressure. To determine the stable phase coexisting with the ideal gas, we compare the chemical potential of considering phases. The illustration of this procedure is shown in Figure 2.2.

Results

Phase diagram

We first investigate the phase behaviour of the system with $\kappa = 3\sigma^{-1}$ for different h . We perform floppy box Monte Carlo (MC) simulations with the potential in Eq.2.1 and 2.2 in isothermal-isobaric ensemble and periodic boundary conditions in x and y directions [69], in which the screened Coulomb potential is truncated at $r_{cut} = 3.5\sigma$. By quenching the simulation to $T^* \rightarrow 0$ at various h , we find three candidate ground states as shown in Figure 2.1 b-d. When $T^* \rightarrow 0$, at low pressure, the system may form NaCl-like (simple cubic) structures confined between two walls, and with increasing pressure P , it switches to be confined CsCl-like (body-center-cubic) structures and CuAu-like (face-centered-cubic) structures at high density. With these candidate crystal structures, we employ the Einstein integration method [65] combined with thermodynamic integrations to calculate the free energy of crystals in confinement [17, 21]. We compare the free energy of crystals with those of the fluid phase obtained from Widom's insertion method [70] to construct the phase diagrams at $h/\sigma = 1, 2.3$ and 4.3 as shown in Figure 2.3 a-c.

When $h/\sigma = 1$, the confined system is exactly in 2D. As shown in Figure 2.3 a, at the low density limit, because of entropy, the stable phase is always a disordered fluid. With increasing the density, crystals form. At large T^* , the fluid crystallizes into a hexagonal crystal with disordered particle charges, and when decreasing T^* , a few charge-ordered crystals appear in the phase diagram. For $T^* \lesssim 0.4$, an ordered binary square crystal nucleates from the fluid at low

FIGURE 2.3: Phase diagrams in the representation of η versus T^* for oppositely charged colloids confined between parallel hard walls with various separation $h/\sigma = 1$ (a), 2.3 (b), and 4.3 (c), where $\kappa = 3\sigma^{-1}$. The area between phases indicates the two-phase coexistence region. (d) The ground-state phase diagram for confined systems of oppositely charged colloids in the representation of h/σ versus $\kappa\sigma$ at $T^* = 0$.

pressure, and with increasing pressure, the high density charge-ordered hexagonal crystal emerges. The stability of the square crystal persists to $T^* \rightarrow 0$, as the square crystal is the energetically most favoured crystal of the system in 2D. Similar behaviour of the system at $h/\sigma = 2.3$ is shown in Figure 2.3 b, in which a 2-layer NaCl-like crystal is more stable than the high density 2-layer CsCl-like crystal at $T^* \rightarrow 0$ because of the fact that the low density crystal is more energetically favoured. It is known that in 3D systems of oppositely charged colloids, CsCl is more stable than NaCl [18], which suggests that at large enough h , the stable multilayer NaCl should disappear. Therefore, we calculate the phase diagram for the confined system of oppositely charged colloids with $h/\sigma = 4.3$ in Figure 2.3 c. One can see that the stability of 4-layer NaCl crystal at $T^* \rightarrow 0$ disappears, while the stable coexistence of 4-layer NaCl crystal with low density fluid still exists in the low temperature range $0.05 \lesssim T^* \lesssim 0.2$.

In Figure 2.3 d, we show the the ground-state phase diagram for confined

FIGURE 2.4: The entropy difference $\Delta S/Nk_B = (S_{4L-NaCl} - S_{5L-CsCl})/Nk_B$ and the enthalpy difference $\Delta H/Nk_B T = (H_{4L-NaCl} - H_{5L-CsCl})/Nk_B T$ as functions of T^* at the pressure where the fluid becomes unstable in the confined oppositely charged colloids with $\kappa = 3\sigma^{-1}$ and $h = 4.3\sigma$. Here $S_{4L-NaCl(5L-CsCl)}$ and $H_{4L-NaCl(5L-CsCl)}$ are the entropy and enthalpy of 4-layer NaCl-like (5-layer CsCl-like) crystal, respectively.

systems of oppositely charged colloids, and one can see that for $\kappa = 3\sigma^{-1}$, when $h/\sigma \gtrsim 3.5$, the multi-layer NaCl-like crystals becomes unstable with respect to the multi-layer CsCl-like crystals, and the maximal stable layers of NaCl-like crystals at the ground state is 3, which decreases with increasing κ . This agrees with our phase diagram in Figure 2.3 c, in which the stable 4-layer NaCl-like crystal disappears at $T^* \rightarrow 0$. In Figure 2.4, in order to understand the stability of 4-layer NaCl-like crystal at low temperature, we plot the entropy difference $\Delta S/Nk_B$ and enthalpy difference $\Delta H/Nk_B T$ between 4-layer NaCl-like and 5-layer CsCl-like crystals in the confined system with $h/\sigma = 4.3$ at the pressure where the fluid becomes unstable for various T^* . Here the 5-layer CsCl-like crystal is the stable ground-state phase. One can see that for the entire range of $0 < T^* \leq 0.2$, ΔS and ΔH are always positive. This implies that vibrational entropy in the confined NaCl-like crystal is larger than that in the confined CsCl-like crystal, which is enthalpically more favoured. Depending on the sign of the Gibbs free energy difference between the two crystals, i.e. $\Delta G = \Delta H - \Delta S T$, one can identify the stable phase. At $T^* \rightarrow 0$, the enthalpy determines the stability $\Delta G > 0$, i.e.

$\Delta H > \Delta ST$, and the first crystal nucleating from the low density fluid is the CsCl-like crystal. However, when $T^* \gtrsim 0.05$, $\Delta G < 0$, i.e. $\Delta H < \Delta ST$, which implies that the large vibrational entropy stabilizes the NaCl-like crystals against the enthalpically favoured CsCl-like crystal. This explains the stability of 4-layer NaCl-like crystal at finite low T^* in Figure 2.3c, which is essentially an entropically stabilized low temperature solid phase of open crystalline structure. This effect is similar to the entropy stabilized open crystals of patchy colloids [42, 43].

FIGURE 2.5: Low temperature phase diagrams at $T^* = 0.1$ for confined oppositely charged colloids in the representation of h/σ versus η with various inversed screening length $\kappa\sigma = 3$ (a), 4 (b) and 6 (c).

Next we calculate the low temperature phase diagrams at $T^* = 0.1$ for oppositely charged colloids confined between two parallel hard walls of different separation h for various κ . As shown in Figure 2.5, at high density the stable phase always has the body-center-cubic (BCC), i.e., CsCl, face-center-cubic (FCC), i.e. CuAu, or multilayer rhombic symmetry, which agrees with the phase behaviour of confined hard spheres at high pressure [17]. When decreasing the density of system, different low density phases appear in the phase diagrams in Figure 2.5. One can see that when $\kappa = 3\sigma^{-1}$, with increasing h/σ from about 2 to 4.5, the low density crystal phase always has the simple cubic symmetry, and the number of layers depends on the confinement height h , in which the maximal layers of stable simple cubic (NaCl) crystals at $T^* = 0.1$ and $\kappa = 3\sigma^{-1}$ is four. As shown in Figure 2.5b and c, the maximal layers of simple cubic crystals decreases with increasing κ , which agrees qualitatively with the confined system at ground state (Figure 2.3d). However, because of the effect of vibrational entropy, the maximal layers of stable simple cubic (NaCl) crystal at finite low temperature could be larger than that at the ground state.

Photonic bandgaps of multi-layer simple cubic crystals

FIGURE 2.6: (a) Side view of optical simulation of normal incident lights with the frequency $\omega a / 2\pi c = 0.392$ upon an inverse 1-, 2-, 3- and 4-layer simple cubic crystal of $a/\sigma = 5/6$ with σ and a are the size of spherical bubble and the lattice constant of the crystal, respectively. The color represents the intensity of the magnetic field (A/m). (b) Transmission spectra of inverse 4-layer (red), 3-layer (blue), 2-Layers (green) and mono-layer (purple) simple cubic crystals planar lights at $a/\sigma = 5/6$ and $\epsilon_r = 6.0$. (c) The band structure along $\Gamma - X$ direction, i.e., the direction perpendicular to the square plane, in the inverse simple cubic crystals with $a/\sigma = 5/6$ and $\epsilon_r = 6.0$. Inset: the Brillouin zone of the simple cubic crystal [71].

Furthermore, we investigate the photonic property of obtained multi-layer simple cubic crystals. We first construct an inverse multi-layer simple cubic crystal, in which the spherical air bubbles of diameter σ form a multi-layer simple cubic crystal with the lattice constant $a/\sigma = 5/6$. Experimentally, these inverse crystals can be obtained by selectively removing the colloidal particles after infiltrating the space between colloids using materials with the dielectric contrast ϵ_r , in which the colloidal spheres are slightly overlapped, by sintering the particles in the crystal [72]. We perform optical simulations with a normal incident light source on one side of the confined crystal. One can obtain the distribution of magnetic field $\mathbf{H}(\mathbf{r}, t) = \mathbf{H}(\mathbf{r})e^{i\omega t}$ by numerically solving the simplified Maxwell equation in the frequency domain with the Floquet periodic boundary conditions in $x - y$ directions [73].

FIGURE 2.7: Heat map of transmittance for the 4-layer simple cubic crystal in the representation of $\omega a/2\pi c$ versus ϵ_r at $a/\sigma = 5/6$. Solid lines enclose the photonic bandgap regions of the bulk simple cubic, FCC and BCC crystals in the direction perpendicular to the confining walls, i.e., the shadow planes in Figure 2.1b-d.

$$\nabla \times \left[\frac{1}{\epsilon(\mathbf{r})} \nabla \times \mathbf{H}(\mathbf{r}) \right] = \left(\frac{\omega}{c} \right)^2 \mathbf{H}(\mathbf{r}) \quad (2.10)$$

where c and ω are the speed and frequency of light, respectively. The resulting $\mathbf{H}(\mathbf{r})$ for inverse multi-layer simple cubic crystals with $a/\sigma = 5/6$, $\omega a/2\pi c = 0.392$, and $\epsilon_r = 6$ is shown in Figure 2.6a. With this, we calculate the transmittance of light with different frequency through the crystal by constructing perfectly matched layers [74] on the top and bottom of the simulation box to absorb the excess reflected and transmitted light. The obtained transmission spectra of multi-layer inverse simple cubic crystal with $\epsilon_r = 6$ is shown in Figure 2.6b. Compared with the corresponding band structure of the bulk simple cubic crystal in $\Gamma - X$ direction (Figure 2.6c), i.e. the direction perpendicular to the confining plane [75], with

increasing the number of layers, the transmittance forbidden region approaches the band gap in the bulk simple cubic crystal, and the 4-layer simple cubic crystal can already almost reproduce the photonic band gap in the bulk simple cubic crystal.

In Figure 2.7, we plot the heat map of the transmittance for 4-layer simple cubic crystal in the representation of $\omega a/2\pi c$ versus ϵ_r . Compared with the band gap obtained in the bulk simple cubic crystal in $\Gamma - X$ direction, one can see that the transmittance forbidden region for the 4-layer simple cubic crystal persists to the low dielectric contrast $\epsilon_r \simeq 4$ close to the photonic band gap of the corresponding bulk crystal. For comparison, we also calculate the band gaps for bulk CsCl (BCC) and CuAu (FCC) crystals in the direction perpendicular to the confinement in Figure 2.6c. Compared to the band gaps of FCC and BCC crystals, the band gaps for multi-layer simple cubic crystals are much larger and open at low frequency range, i.e., $0.2 \leq \omega a/2\pi c \leq 0.5$, suggesting that they are robust against disorder [76].

Conclusion

To conclude, by using computer simulation, we have investigated the self-assembly of oppositely charged colloids confined in two parallel hard walls, in which we found stable multi-layer simple cubic crystals. With decreasing the inverse screening length κ , the number of layers of stable confined simple cubic crystals increases, and with $\kappa = 3\sigma^{-1}$, at low temperature, one can stabilize upto 4-layer simple cubic crystal, of which the inverse structure has large photonic band gaps open at low frequency with the dielectric contrast as low as $\epsilon_r \simeq 4$. This suggests new possibilities of fabricating photonic devices using low dielectric contrast materials like TiO_2 ($\epsilon_r \simeq 6.8$), SiC ($\epsilon_r \simeq 7.3$), ZnS ($\epsilon_r \simeq 5.6$), GaN ($\epsilon_r \simeq 5.8$), ZnO ($\epsilon_r \simeq 5.8$), silica ($\epsilon_r \simeq 3.9$), etc., which were difficult for conventional colloidal self-assembly methods.

Chapter 3

Nucleation of multi-layer simple cubic crystals of Confined oppositely charged colloids

Introduction

Crystallization processes ubiquitously exist in both nature and synthetic systems for which atoms or molecules in the systems orderly form a solid phase called a crystal from a fluid phase. These processes start with the formation of crystalline nuclei, small clusters, from a supercooled liquid or superstaturated solvent followed by the growth of these clusters to a crystal phase. The nucleation step is the process-limiting step since the further growth of the clusters to a crystalline phase requires a nucleus to overcome the barrier at which the nucleus size is large enough to continually crystallize the surrounding fluid. In general, small nuclei form spontaneously in a supersaturated fluid and melt back to fluid and only a small fraction of these nuclei can propagate its growth. The simplest theory to describe this process is classical nucleation theory (CNT) which assumes that the free energy of forming a small nucleus results from a bulk free energy which is proportional to the volume of the nucleus and a surface energy that is proportional to the surface area of the formed cluster. By assuming that a nucleus arises from a homogeneous supercooled liquid has spherical shape of radius R , one can write down the Gibbs free energy difference between the host bulk fluid and the nucleus as:

$$\Delta G = \frac{4}{3}\pi R^3 \rho_S \Delta\mu + 4\pi R^2 \gamma \quad (3.1)$$

where R is the radius of a spherical nucleus, ρ_S is the number density of the solid, $\Delta\mu$ the difference in chemical potential of the solid and the fluid phases ($\Delta\mu < 0$ for a supersaturated system), and γ is the solid-fluid interfacial free energy density. In the presence of confining walls, the nucleation process here is heterogeneous and the nucleation barrier is much lower than its bulk process due to the smaller surface area of the nucleus as parts of it are accommodated by the wall surfaces [77].

Since the nucleation process is a rare event, umbrella sampling [78] has been widely implemented to obtain the nucleation barrier. In this scheme, a system is biased towards desired regions in the configuration space by choosing an order parameter that is able to identify specific crystalline structures and ensemble averages on configurations resulting from the choice of the order parameter are determined.

From the previous chapter, the phase diagram in Figure 2.3 shows that the 4-layers simple cubic crystal confined between two flat walls with the gap separation of $H = 4.3\sigma$ has the widest stable region at reduced temperature $T^* = 0.15$ with the inverse Debye screening length $\kappa = 3\sigma^{-1}$. The equation of state of the system at this region is illustrated in Figure 3.1. The coexistence of the fluid and the 4-layers simple cubic is shown by the blue dashed line drawn at the pressure $\beta P\sigma^3 = 1.382$ which refers to $\eta_{fluid} = 0.3459$ and $\eta_{4L-NaCl} = 0.4236$. In this chapter we focus on studying the nucleation process of the 4-layers simple cubic crystal from the disorder fluid phase at the supersaturation region slightly higher than this coexisting point, i.e. $1.50 \leq \beta P\sigma^3 \leq 1.71$. Here we observed that the nucleus initially forms at the wall surfaces and bilaterally grows in both vertical direction inwards the bulk and horizontal direction in $x-y$ plane. This observation is confirmed by determining the density profile. The calculated Gibbs free energy barrier in this supersaturation region shows the discrepancy when fit with the CNT assuming the spherical shape of the nucleus while the fit with the cylindrical nucleus shape assumption shows the better alignment with the simulation results. This points out the effect of the boundaries on nucleation processes.

FIGURE 3.1: Equations of states, i.e. Pressure $\beta P \sigma^3$ as function of packing fraction $\eta = \pi \sigma^3 N / (6Ah)$ where A is the the area of the system in $x - y$ plane of the Fluid (black), 4-layers Simple cubic (NaCl) crystal (green) and 5-layers body-centered cubic (CsCl) crystal (red) phases in a system of oppositely charged colloids confined between two planar hard walls separated by a distance $H/\sigma = 4.3$. The blue dashed line indicates the region where the fluid and 4-layers simple cubic crystal phases coexist.

Methodology

Model

In this chapter, we study the nucleation of the system of N confined oppositely charged spheres with diameter σ whose inter-particle interaction is given by the screened Coulomb pair potential [63]

$$\frac{U(r_{ij})}{k_B T} = \begin{cases} \pm \frac{Z^2}{(1+\kappa\sigma/2)^2} \frac{\lambda_B}{\sigma} \frac{e^{-\kappa(r-\sigma)}}{r/\sigma} & r \geq \sigma \\ \infty & r < \sigma \end{cases} \quad (3.2)$$

where r_{ij} is the center-to-center distance between two particles and $\lambda_B = e^2/\epsilon_s k_B T$ is the Bjerrum length with ϵ_s the dielectric constant of the solvent. k_B and T are the Boltzmann constant and the temperature of the solvent, respectively. The inverse Debye screening length $\kappa = \sqrt{8\pi\lambda_B\rho_{salt}}$ where ρ_{salt} the salt concentration is set to $\kappa = 3\sigma^{-1}$. Half of particles carry a positive charge Ze , and the other half a negative charge $-Ze$. The confining walls have the gap separation of $h = 4.3\sigma$ with the area of each side $A = L_x L_y$. We also define $T^* = (1 + \kappa\sigma)^2\sigma/Z^2\lambda_B$ as the reduced temperature, i.e., the inverse of the contact value of the potential in Eq.3.2. The illustration of the system can refer to Figure.2.1a).

Umbrella sampling

In this chapter, the umbrella sampling scheme is used to calculate nucleation barriers. This method was, first, proposed to improve sampling of a system where the Boltzmann factor is small [78]. This method has been applied to study rare events such as nucleation [79–81]. Principally, this scheme is used to investigate the region of configurational space where traditional schemes, e.g. Metropolis Monte Carlo simulations, are inaccessible since, in general, the potential barrier is too high to overcome. In umbrella sampling, the standard Boltzmann weighting is added by a bias potential which forces the system to oversample in a desired region of the configurational space. The ensemble average in Eq.1.19 is, then, can be reviewed as

$$\begin{aligned} \langle A \rangle_{NPT} &= \frac{\int dV \int d\mathbf{r}^N A(\mathbf{r}^N) \exp[-\beta(U(\mathbf{r}^N) + PV)] W(\mathbf{r}^N)^{-1} W(\mathbf{r}^N)}{\int dV \int d\mathbf{r}^N \exp[-\beta(U(\mathbf{r}^N) + PV)] W(\mathbf{r}^N)^{-1} W(\mathbf{r}^N)} \\ &\times \frac{Q(N, P, T)}{Q(N, P, T)} = \frac{\langle A/W(\mathbf{r}^N) \rangle_{bias}}{\langle 1/W(\mathbf{r}^N) \rangle_{bias}} \end{aligned} \quad (3.3)$$

where $W(\mathbf{r}^N) = \exp[\beta U_{bias}(\mathbf{r}^N)]$ and U_{bias} is the biasing potential. So, instead of simulating with the original Boltzmann weight, we now examine the phase space by using the biased distribution function $\exp[-\beta U(\mathbf{r}^N) + PV] W(\mathbf{r}^N)$, which is denoted by the subscription $\langle \dots \rangle_{bias}$. Typically, the biasing potential is chosen to be an

harmonic function of the number of particle of the largest cluster in the system

$$\beta U_{bias}[n(\mathbf{r}^N)] = \frac{1}{2}k_n[n(\mathbf{r}^N) - n_0]^2 \quad (3.4)$$

where k_n is a coupling parameter which in this study we set at $k_n = 0.2$, $n(\mathbf{r}^N)$ is the size of the largest cluster of the configuration $\mathbf{r}^N$, and n_0 is the desired cluster size. The constant k_n determines the range of sample sizes measured in a simulation. By carefully choosing the k_n , the sampling will fluctuate only around the size of n_0 as shown in Figure 3.2. As one can clearly see that the sampling of each Monte Carlo run is fluctuated around the targeted n_0 which exhibits the nearly Gaussian distribution.

FIGURE 3.2: Distribution function of the largest cluster size from biased NPT simulations run in the range of $n_0 \in [10 - 250]$ particles.

For studying nucleation, we need to calculate the ensemble average owing to the biased ensemble, Eq.3.3, as

$$\langle N_n \rangle_{NPT} \approx \frac{\sum_i^M (N_n(\mathbf{r}_i^N) / W(\mathbf{r}_i^N)^{-1})}{\sum_i^M W(\mathbf{r}_i^N)^{-1}} \quad (3.5)$$

where subscription n denotes the sampled cluster size. We, then, calculate the free energy barrier by

$$\beta \Delta G(n) = \text{const.} - \ln[P(n)] \quad (3.6)$$

The $P(n) = \langle N_n \rangle / N$ is the probability distribution function of finding a cluster with size n .

Order Parameter

In order to differentiate between fluid-like and solid-like particles, we used a local bond-order parameter introduced by Ten Wolde et al. [82]. The advantage of using this order parameter is its sensitivity to the degree of crystallinity in the system but independent to crystal structures. This order parameter is fundamental for applying the biasing potential since we use the parameter to force the system to crystallize to a desired structure.

To calculate the local bond order parameter, we have to determine a list of neighboring particles for each particle i within a distance r_c from particle i . The bond order parameter of each particle can be, then, calculated from

$$q_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |q_{lm}(i)|^2} \quad (3.7)$$

where l is a free interger parameter $l = 0, 1, 2, \dots$, $q_{lm}(i)$ is a complex vector of particle i which is defined as

$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(r_{ij}) \quad (3.8)$$

The $N_b(i)$ is the number of nearest neighbors in the list of particle i , r_{ij} is the normalized direction vector between particle i and j and m is an integer which runs from $m = -l$ to $m = +l$. The function $Y_{lm}(r_{ij})$ is the spherical harmonics. Here in this study we set $l = 6$ and we calculate the correlation function of the vector q_6 of particles i and j as

$$q_6(i) \cdot q_6(j) = \sum_{m=-6}^6 q_{6m}(i) \cdot q_{6m}(j)^* \quad (3.9)$$

FIGURE 3.3: Distribution function of the dot product of the local bond-order parameter between particle i and j , $q_6(i) \cdot q_6(j)$ from Monte Carlo simulation in a confined oppositely charged system. The dot-products are normalize to one.

where the superscription $*$ denotes the complex conjugate. In Figure.3.3, the distribution function of the structures found in the confined oppositely charged system is plotted. The dot product of the solid structures, NaCl and CsCl, show higher values compared to that of the fluid. From this plot, we now can set the threshold for the dot product $q_6(i) \cdot q_6(j) = 0.5$ which defines as when the dot-product

exceeds this threshold, the two considering particles are neighbours. Now we can use this criterion to identify all solid-like particles in the system. Next we have to determine whether the solid-like particle belongs to a cluster by setting a cutoff distance between two solid-like particles $r_c = 1.4\sigma$. If the two particles distance less than this threshold, then they belong to the same cluster.

Results

FIGURE 3.4: Configurations of simple cubic crystal nucleation from a disordered supersaturated fluid phase in an NPT biased-Monte Carlo simulation at $\beta P \sigma^3 = 1.66$. The top panel shows the top view while the middle and bottom panels show the front view. The bias towards cluster sizes of (A,E) $N_0 = 15$, (B,F) $N_0 = 36$, (C,G) $N_0 = 85$ and (D,H) $N_0 = 222$ particles. The different colors represent different particle charges and particles which not belonging to the largest cluster are in small sizes.

In this chapter, we mainly focus on studying nucleation of the confined system. Thus, it is worth to begin with the role of the confining walls in nucleation process. Here we investigate the nucleation process of the fluid phase to a 4-layer simple cubic crystal at wall separation $h = 4.3\sigma$. The packing fractions used in simulations range from $\eta \in (0.351, 0.432)$ which corresponds to the pressure range of $\beta P \sigma^3 \in (1.40, 2.04)$. Note that we set the range of pressures used in

simulation slightly higher than the coexisting pressure between fluid-simple cubic crystal which equals $\beta P\sigma^3 = 1.382$. By implementing the bond order parameter stated above, we can distinguish between fluid-like and solid-like particles. Figure 3.4 shows the evolution of the simple cubic nucleus in the host fluid phase at pressure $\beta P\sigma^3 = 1.66$. As one can clearly see from the side-view snapshot in Figure 3.4(E-H), the nucleus starts to form at the surface of the confining walls and induces the crystallization of particles inwards to the center of the confined fluid. This process is a bilateral, occurs both inwards the center and expands in x-y plan simultaneously. The top panel of Figure 3.4 shows the top view for this nucleation process. As the nucleus grows, the phase at the center of the nucleus becomes more ordered, Simple cubic structure, with the disordered particles at the interface, refers to the Figure 3.4A) to Figure 3.4D) as the time propagates. The simplest way to illustrate the effect of confining wall on this nucleation process is to determine the density profile of the particles confined between two hard walls. This density profile is simply defined as the average number of particle in small stack of height Δh , $\langle \rho(Z) \rangle = \langle N_z \rangle / (\Delta h L_x L_y)$. Figure 3.5 shows the calculated density profile as function of position in z-direction at the $\beta P\sigma^3 = 1.70$ where the nucleation can spontaneously occur after MC steps. One can clearly see that after 600000 MC steps, the density profile value at the surface of the confining walls is greater than that at the center of the system. This refers to the formation of the nucleus at the surface of the confining walls, Figure 3.4E). After some MC steps, the value of the bulk, middle of the confining system, increases along with the increase of the value at $Z = 0.5\sigma$ and $Z = 3.8\sigma$ which indicates the bilateral growth into the center of the slab and outwards in x-y plan. Eventually, when the crystallization occurs throughout the simulation box, the density profile value at $Z = 0.5\sigma$ and $Z = 3.8\sigma$ are nearly equal to the value at $Z = 1.6\sigma$ and $Z = 2.7\sigma$. By plotting the number of fluid-like and solid-like particles as shown in Figure 3.6 at the pressure, one can clearly see that after $\approx 4 \times 10^6$ MC steps

FIGURE 3.5: Density profile of the oppositely charged particle confined between two hard walls as function of distance in z -direction at pressure $\beta P \sigma^3 = 1.70$ after 600000, 4800000, 5700000 and 6000000 MC steps

the largest cluster size of ≈ 80 particles forms and leads the spontaneous nucleation throughout the phase space which refers to the jump in number of simple cubic-like particles and the drop in the number of fluid-like particles. Next, we apply the umbrella sampling scheme stated in previous section to determine the Gibbs free-energy barriers. As shown in Figure 3.7, the study were carried out at pressures $\beta P \sigma^3 = 1.58, 1.624, 1.628$ and 1.6633 . These points correspond to the supersaturation of $\beta |\Delta \mu| = \beta |\mu_{Simplecubic} - \mu_{Fluid}| = 0.339, 0.407, 0.413$ and 0.466 . At the higher supersaturations than this regime, the nucleation process can spontaneously occur, as shown in Figure 3.4 and 3.5. As the figure shows, once the pressure of the system increases, the nucleation barrier becomes flatter. The paramount of each barrier refer to the $\Delta \beta G_{crit}$ and the critical nucleus size. From the figure, $\beta P \sigma^3 = 1.58, 1.624, 1.628$ and 1.6633 display the maximum of

FIGURE 3.6: Number of fluid-like and simple cubic-like particles versus simulation time (MC step) at pressure $\beta P \sigma^3 = 1.70$ from typical Monte Carlo simulations.

$\Delta\beta G_{crit} \approx 15.6, 15.1, 14.57$ and 13.0 at critical cluster sizes $n_{crit} \approx 110, 90, 110$ and 80 , respectively. To further investigate on the shape of the nucleus, we fit the calculated Gibbs free-energy barriers with the classical nucleation theory (CNT). The typical expression of this theory with the assumption that a nucleus has the shape of sphere is written down in Eq.3.1. By expressing $n = 4\pi R^3 \rho_S / 3$, we can rewrite Eq.3.1 in terms of cluster size as:

$$\Delta G_{sphere} = n\Delta\mu + (4\pi)^{\frac{1}{3}} \left(\frac{3n}{\rho_S} \right)^{\frac{2}{3}} \gamma \quad (3.10)$$

The result of this fitting is shown in Figure 3.8a). One can clearly see the large discrepancy between the fitting model (solid lines) and the numerical results (dots), and especially the CNT cannot even fit the paramount of the barriers. We, then,

FIGURE 3.7: Gibbs free-energy barriers $\beta\Delta G(n)$ of confined oppositely charged colloids as a function of cluster size n obtained from umbrella sampling MC simulations at reduced pressures $P\beta\sigma^3 = 1.58, 1.624, 1.628$ and 1.6633 as labelled.

FIGURE 3.8: Gibbs free-energy barriers $\beta\Delta G(n)$ of confined oppositely charged colloids as a function of cluster size n obtained from umbrella sampling MC simulations at reduced pressures $P\beta\sigma^3 = 1.58, 1.624, 1.628$ and 1.6633 as labelled fitted with the classical nucleation theory (CNT) assuming the shape of nucleus as a) sphere and b) cylinder.

re-assume the shape of the nucleus to a cylindrical shape since the nucleated simple cubic structure is confined between two flat walls and from the snapshots in Figure 3.4 shows that, from the top view, the forming nucleus is rather formed into a circular shape. Thus, replacing the spherical volume and surface area in Eq.3.1 with a cylindrical one, we arrive:

$$\Delta G = \pi R^2 h \rho_S \Delta \mu + (2\pi R h + 2\pi R^2) \gamma \quad (3.11)$$

where h is the gap separation between two confining walls, $h = 4.3\sigma$. By expressing $n = \pi R^2 h \rho_S$, we can, again, rewrite Eq.3.11 in terms of cluster size as:

$$\Delta G_{sphere} = n \Delta \mu + \left[2 \left(\sqrt{\frac{n \pi h}{\rho_S}} \right) + 2 \left(\frac{2n}{\rho_S h} \right) \right] \gamma \quad (3.12)$$

The fitting result by Eq.3.12 is shown in Figure 3.8b). Now, the fitting lines decently align with the simulation results. This implies that the boundaries, at the confining walls, introduce effects on the nucleation process which results in changing the nucleus shape from the sphere in bulk system to cylindrical shape in the confined system. The only dissimilarity between CNT assuming spherical nucleus shape in Eq.3.10 and the cylindrical one in Eq.3.12 is the surface term. For the spherical case, the surface term is the function of, only, number of particle in the nucleus and its density while in the cylindrical case the surface term is also the function of the confining walls separation. This can explain why the later case can better cope the phenomena occur under the confinement. We also note the small discrepancies for the cylindrical fitting which may refer to the nature of the cylinder that comprises flat surfaces rather than a curved surface. The fitting parameters are listed in Table 3.1.

Conclusion

In conclusion, we systematically examine the nucleation process of 4-layers simple cubic crystal in oppositely charged colloidal system confined between two flat walls by implementing the umbrella sampling method. The NPT biased-Monte Carlo

$\beta P \sigma^3$	ρ_{Fluid}	ρ_{NaCl}	$\beta \Delta\mu $	$\beta \gamma_{sphere} \sigma^2$	$\beta \gamma_{cylinder} \sigma^2$
1.580	0.6821	0.8139	0.3386	0.413	0.354
1.624	0.6868	0.8148	0.4069	0.450	0.400
1.628	0.6871	0.8149	0.4130	0.458	0.401
1.663	0.6908	0.8157	0.4659	0.475	0.422

TABLE 3.1: Numerical values for the parameters affiliated with the fits in Figure 3.8, density of fluid and simple cubic phases, chemical potential difference between the fluid and solid phases, interfacial free-energy density of both spherical and cylindrical nucleus at given pressures, using classical nucleation theory assumed spherical and cylindrical shape of the nucleus, a) and b) respectively.

simulation shows that the nucleus initially forms at the confining wall surfaces and bi-axially grows in vertically, inwards the bulk of the confining slap, and horizontally in the $x-y$ plane. The density profile plot as a function of confinement height at the pressure where the nucleation can spontaneously occurs confirms this wall wetting phenomenon. The calculated Gibbs free-energy barriers in supersaturation region $0.33 \leq \beta |\Delta\mu| \leq 0.47$ show that by fitting the simulation results with the classical nucleation theory assuming the spherical shape of the nucleus, the large discrepancy signifies while fitting with assuming cylindrical shape shows the better agreement. This can be caused by the surface term difference of both shapes where the cylindrical surface term is also a function of the confinement parameters while the spherical one is only a function of cluster size and its density. This highlights the effect of the boundaries on nucleation processes.

Chapter 4

Confinement Induced BCC-FCC Phase Reentrances in Thin Colloidal Films

Introduction

Colloidal self-assembled thin film are ubiquitously used in broad range in modern technologies, e.g., light harvesting [83, 84], membrane [85], pH optical sensors [86] or coatings [87] .

In hard-sphere systems, confining thin-layers of such particles with hard walls can demonstrate an interesting phase diagram with the well-known sequence $\dots n\Delta \rightarrow (n+1)\square \rightarrow (n+1)\Delta \dots$, with n the number of crystal layers, with increasing the plate separation with some intermediate structure, e.g. buckle, rhombic and prism, which is absent in the bulk system. This behavior is purely entropy driven [17, 88].

In case of charge repulsive systems, e.g. dusty plasmas, the interparticle-interaction is described by an intermediate screened coulomb or Yukawa pair potential owing to the screening by additional micro-ions in the system. Experimentally, the screening length can be altered by changing the micro-ion concentration, e.g. adding salt ions to the aqueous suspensions in the case of charged colloids. Even though many of simulations and its following experimental studies have been conducted at **zero temperature** for bilayers Yukawa particles [56, 89] and the results show quite similar behavior with hard-sphere systems, observed the square-triangle reentrance with some intermediate structures. The further study [90] which mainly focus on the transition from $2\Delta \rightarrow 3\square$ reports many intermediate phases including the novel

phase, Belgian waffle iron(BWI). However, the full picture of the transition from a 2D crystal to a 3D crystal is still in mist.

For the purely repulsive potential, fluid phase can freeze into a solid with either a Face-Centered-Cubic (FCC) or a Body-Centered-Cubic (BCC) structure. It is worth to study in detail of the transition between these phases. The phase diagram of the bulk hard-core repulsive Yukawa particles has been reported [4]. Introducing the walls to confine the system can, probably, alter the behavior of the system. In this chapter by systematically investigate both experimentally and by simulation, we find the peculiar behaviour of BCC-FCC reentrance of the self-assembly of repulsive Yukawa colloidal sphere confined between two hard walls in the regime of BCC stable in the bulk system. This reentrance is different from the confined hard-sphere system. We are able to observe the reentrance up to 14 layers where the FCC phase becomes rare and the bulk ground state, BCC, is recovered.

Methodology

Model

Our system comprises of N repulsive colloidal particles in which the interparticle-interaction is the pairwise repulsive Yukawa potential, including the hard-core interaction, confined between two walls with separation gap h . We emphatically study on free energy calculation of the existing phases. The pair potential between colloids i and j is given by

$$\frac{U(r_{ij})}{k_B T} = \begin{cases} \beta \epsilon \frac{e^{-\kappa(r-\sigma)}}{r/\sigma}, & r \geq \sigma \\ \infty, & r < \sigma \end{cases} \quad (4.1)$$

where r_{ij} is the distance between two particles measured from their center of mass, $\beta \epsilon$ is the contact value of the pair potential per $k_B T$, with k_B and T the Boltzmann constant and the temperature of the solvent, respectively, and $\kappa = \sqrt{8\pi\lambda_B\rho_{salt}}$ is the inverse Debye screening length with ρ_{salt} the salt concentration. By applying

the Derjaguin-Landau-Verwey-Overbeek pair potential [63], the contact value can be expressed as

$$\beta\epsilon = \frac{Z^2}{(1 + \kappa\sigma/2)^2} \frac{\lambda_B}{\sigma}, \quad (4.2)$$

where Z is the charge of the colloids and $\lambda_B = e^2/\epsilon_s k_B T$ is the Bjerrum length of the solvent with dielectric constant ϵ_s . In order to map our confined system with the set of parameters used in the earlier results obtained for the bulk Yukawa system [4], here we characterize the system by the dimensionless temperature

$$\tilde{T} = \left[\frac{2}{3} \lambda^2 \beta U_0 u_M(\lambda) \right]^{-1} \quad (4.3)$$

The inverse screening length λ is in unit of the characteristic interparticle separation length scale $a = \rho^{-1/3}$ and u_M is the Madelung energy of an ideal fcc crystal per particle per βU_0 . By using this length scale, the described Yukawa pair potential in Eq.4.1 can be rewritten as

$$\beta u(r) = \beta U_0 \frac{e^{(-\lambda r/a)}}{r/a} \quad (4.4)$$

where βU_0 is a constant prefactor. By coupling the Eq.4.1 for $r > \sigma$ and Eq.4.4, we obtain the relationship between simulation parameters

$$\begin{aligned} \kappa &= \lambda/a, \\ e^{\kappa\sigma} \sigma \epsilon &= \beta U_0 a. \end{aligned} \quad (4.5)$$

Using the fact that $a = (6\eta/\pi)^{1/3} \sigma$, the Eq.4.5 can be rewritten as

$$\begin{aligned} \beta U_0 &= e^{\kappa\sigma} \beta \epsilon (6\eta/\pi)^{1/3}, \\ \lambda &= \kappa \sigma (6\eta/\pi)^{-1/3} \end{aligned} \quad (4.6)$$

We assume the neutral confining walls and the interaction between particle i and the confining walls is dominated by the excluded volume effect

$$U_{wall-fluid} = \begin{cases} 0 & r_i \geq \sigma/2 \\ \infty & r_i < \sigma/2 \end{cases} \quad (4.7)$$

where r_i is the distance of the center of mass of particle i to the nearest wall in z direction.

Free energy calculation

To determine the change of free energy as a function of plate separation height h , we adopt the method developed by Frenkel and Ladd [65] which was also implemented in the Chapter2. The Gibbs free energies are calculated using the standard thermodynamic integration technique [21]. The Helmholtz free energy F of a crystal confined between two parallel walls can be written as

$$\begin{aligned} F(N, V, T) &= F_{Einst}(N, V, T) \\ &- \int_0^{\lambda_{max}} d\lambda \left\langle \frac{\partial U_{Einst}(\lambda)}{\partial \lambda} \right\rangle_{\gamma_{max}, 1/T_{max}^*} \\ &+ \int_0^{1/T^*} d(1/T^*) \left\langle \frac{\partial \sum_{i \neq j} U(r_{ij})}{\partial (1/T^*)} \right\rangle_{\gamma_{max}, \lambda_{max}} \\ &+ \int_0^{\gamma_{max}} d\gamma \left\langle \frac{\partial [\sum_{i \neq j} \varphi(i, j) + \sum_i \psi(i)]}{\partial \gamma} \right\rangle_{1/T^*=0, \lambda_{max}} \end{aligned} \quad (4.8)$$

where F_{Einst} is the free energy of the ideal Einstein crystal. $\varphi(i, j)$ and $\psi(i)$ are the soft potentials between particle i and j and particle i with the nearest wall,

respectively:

$$\frac{\varphi(i, j)}{k_B T} = \begin{cases} \gamma[1 - A(1 + \zeta(i, j))] & \zeta(i, j) < 0 \\ 0 & \text{otherwise} \end{cases} \quad (4.9)$$

and

$$\frac{\psi(i)}{k_B T} = \begin{cases} \gamma[1 - A(1 + \zeta(i))] & \zeta(i) < 0 \\ 0 & \text{otherwise} \end{cases} \quad (4.10)$$

where $\zeta(i, j)$ and $\zeta(i)$ are the surface distances between particle i and j and between particle i and its nearest wall, respectively, and they are negative when overlapped. γ is the integration parameter with $A = 0.9$ [66]. Here we choose to use $\gamma_{max} = 150$ to guarantee the hardcore interaction is reproduced at γ_{max} . $U_{Einst}(\lambda)$ is a harmonic potential used to fix the particles onto a perfect crystal lattice:

$$U_{Einst}(\lambda) = \lambda \sum_i (\mathbf{r}_i - \mathbf{r}_{i,0})^2 / \sigma^2 \quad (4.11)$$

where $\mathbf{r}_i$ and $\mathbf{r}_{i,0}$ are the position of particle i and its corresponding position in a perfect lattice, respectively. λ is the integration parameter, and we choose $\lambda_{max} = 2000$. The first term in Eq.4.8 is for an ideal 3D Einstein crystal, of which the free energy is [68]

$$\frac{F_{Einst}(N, V, T)}{N k_B T} = -\frac{3(N-1)}{2N} \ln \left(\frac{\pi}{\lambda_{max}} \right) + \frac{\ln \rho \sigma^3}{N} - \frac{3 \ln N}{2N} \quad (4.12)$$

To calculate the integration in Eq.4.8, we employ the 20-point Gaussian Quadrature integration method. We have ensured that error in the calculated free energy is smaller than $0.01 k_B T$ per particle.

Simulation details

We study the system by employing floppy box Monte Carlo (MC) simulation using the potentials in Eq.4.1 and 4.7 with truncated distance of screened Coulomb potential at $r_{cut}(\kappa)$ in unit of particle diameter σ . Since this cut off distance is a function of the inverse Debye screening length κ and κ itself depends on the inverse screening length λ , we set the truncation r_{cut} at r where the potential in Eq.4.1 decays to $10^{-8}k_B T$ for each λ .

To calculate the free energy of each confinement height h , we need to determine the pressure that the considered phases are stable and apply this pressure throughout the simulations. We start a simulation with a perfect crystal initial configuration. Then we run isothermal-isobaric Monte Carlo ensemble to obtain the pressure by compressing the system and allowing the simulation box shape change in $x - y$ direction where the periodic boundary conditions are applied. The ensemble averages are calculated from runs with $10^4 - 10^5$ MC cycles (attempts to displace N particle once), after first equilibrating the system using ≈ 20000 MC cycles.

Experimental setup

We suspend DiIC₁₈ dyed and polyhydroxystearic acid polymers grafted poly(Methyl Methacrylate)(PMMA) colloids in a mixture of the non-polar solvent (Tetrahydronaphthalene, Aldrich) and the weakly-polar solvent (mixture of Iododecane and Iodododecane, Aldrich), whose refractive index and density are closely matched with those of particles, inside a wedged cell. The inclination angle is 0.16° . The PMMA particles, which have diameter $\sigma = 1.5 \mu m$ with the polydispersity of less than 2.5%, are negatively charged in the solvent. The interaction can be effectively described by the hard-core Yukawa potential as given in Eq.4.1. For this study, the colloidal particle volume fraction is around 17%, where particles do not experience direct contacts and can be safely assumed to interact with the soft repulsive interaction.

We determine the three-dimensional structures with a Leica SP8 fast confocal microscope. The scanning speeds ($\sim 10 \mu m/s$ along z direction, with a $150 \times 150 \mu m^2$ $x - y$ view field) in all dimensions are at least 8 times faster than the Brownian

time ($\sim 1.8\text{s}$), i.e. the time for a particle to freely diffuse over the particle size ($1.5\ \mu\text{m}$), which enables the precise positioning of particles.

Results

FIGURE 4.1: Illustration of (Top panel) Unit cells and (Bottom panel) snapshots of (left) BCC(110), (middle) HCP (0001) and (right) FCC(111). The shadow plane is parallel to the confining walls

Free energy change

Two regimes of the repulsive Yukawa colloidal system in bulk phase diagram [4] which indicate the BCC and FCC stable region are experimentally studied under the confinement. The confined system in FCC stable region, which locates at higher λ , shows the phase behaviour similar to the hard-sphere system [17] with the sequence $\dots n\Box \rightarrow n\Delta \rightarrow (n+1)\Box \dots$. This reentrance behaviour repeats up to ≈ 8 layers then the square phase becomes rare. On the other hand for the BCC stable regime, the phase behaviour is more interesting. Here we find the BCC-FCC reentrance up to 14 layers instead of $\dots n\Box \rightarrow n\Delta \rightarrow (n+1)\Box \dots$ phase reentrance like the hard-sphere system.

To further investigate this behaviour, we performed series of isothermal-isobaric Monte Carlo ensemble, with periodic boundary conditions in x and y directions [69] to predict candidate phases that are stable at different confining heights h . To ensure that we are simulating the system in the BCC stable region, we set the simulation parameters as follow: $\beta\epsilon = 80$, $\lambda \approx 3 - 4$ and $\tilde{T} \approx 0.002 - 0.0025$. We found that the BCC(110), HCP(0001) and FCC(111) phases are stable throughout the simulation parameters, we show later in the free energy calculation part that the FCC is more stable than HCP, and accordingly the simulations show the transition from BCC. The snapshots and unit cells of those phases are illustrated in Figure 4.1. To distinguish the phases, we apply local bond order parameter q_l and w_l which are defined as [91]

$$q_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |q_{lm}(i)|^2}$$

$$w_l(i) = \frac{\sum_{m_1+m_2+m_3=0} \binom{l}{m_1} \binom{l}{m_2} \binom{l}{m_3} q_{lm_1}(i) q_{lm_2}(i) q_{lm_3}(i)}{\left(\sum_{m=-l}^l |q_{lm}(i)|^2 \right)^{3/2}} \quad (4.13)$$

where $q_{lm}(i)$ of particle i is defined as

$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{n_b(i)} Y_{lm}(\mathbf{r}_{ij}) \quad (4.14)$$

In Eq.4.14, $N_b(i)$ is the number of nearest neighbors of particle i , l is a free integer parameter, and m is an integer that runs from $m = -l$ to $m = +l$. The functions $Y_{lm}(\mathbf{r}_{ij})$ are the spherical harmonics and $\mathbf{r}_{ij}$ is the vector from particle i to particle j . In Figure 4.2 we show the distribution of the local bond order parameter q_4 and q_6 and w_4 and w_6 of the system at various h . As one can see, the $q_6 - w_4$ plane can better distinguish between BCC and HCP compared to $q_6 - q_4$ plane.

We further study the free energy change as a function of plate separation height h by using the method stated in the methodology section. Starting with 3L-BCC(110), we compressed the system by allowing the simulation box shape change in

FIGURE 4.2: Scatter plot of the order parameter obtained from NVT simulations of the confined repulsive Yukawa system at various walls separation height in the range of $3.3\sigma \leq h \leq 4.3\sigma$. (a) The plot in $q_4 - q_6$ plan and (b) $w_4 - q_6$ plan. The color of each point represents the height of the confinement

the x-y direction with the periodic boundary conditions applied. We found that at pressure $P\sigma^3/k_B T \approx 42.274$, the BCC phase can stabilize up to $h = 3.2\sigma$ and then transforms to 3L-HCP. Thus, we apply this pressure to further conduct free energy calculations. In Figure 4.3a) and 4.4a), the Gibbs free energy difference are calculated using the standard thermodynamic integration technique.

FIGURE 4.3: Thermodynamic properties of the 3-layers-system as function of confinement height, $h(\sigma)$. The structures plotted here are the structure founded from compressing the system at $P\sigma^3/k_B T = 42.274$ a) Gibbs free energy per particle b) Entropy per particle and c) Enthalpy per particle.

We, first, calculate the free energy of the system of 3-layers crystals for different confinement height, $h(\sigma)$, as shown in Figure 4.3a). Starting from 3L-BCC(110), when h increases to $\approx 3.45\sigma$ the phase transforms to 3L-FCC, as one can see the jump in the free energy plot from the BCC branch (red) to the FCC branch (blue). As we mentioned above, in our simulation we also found the transformation

from BCC to HCP and based on the free energy, the differences between those of FCC and HCP phases are quite small, in the order of $10^{-1}k_B T$ per particle. This transition has been reported in its possibility [92] even though the free energy of the HCP crystal is always higher than that of FCC [93]. For further understanding of the phase behaviours in this regime, we decompose the free energy into entropy TS/N and enthalpy H/N following the relationship $G = H - ST$, Figure 4.3b) and c) respectively. As one can see, the entropy contribution of BCC is greater than that of FCC and HCP. On the other hand, once the confinement height increases, the entropies of FCC and HCP become comparable to that of BCC while the enthalpies of FCC and HCP have the tendency to be lower. This can cause the decrease in free energy of HCP and FCC when the the confinement height increases and induces the phase transition from BCC to FCC.

FIGURE 4.4: Thermodynamic properties of the 5-layers and 6-layers-system as function of confinement height, $h(\sigma)$. The structures plotted here are the structure founded from compressing the system at $P\sigma^3/k_B T = 42.274$ a) Gibbs free energy per particle b) Entropy per particle and c) Enthalpy per particle.

We now further calculate the thermodynamic properties of the system of 5-layers and 6-layers crystals, as shown in Figure 4.4. Unlike the 3-layers crystals case, here we start from 5L-FCC and 5L-HCP in which the free energy of 5L-FCC is lower, consistent with the 3-layers. By decomposing the free energies, we find that the entropy contribution of FCC is greater than that of HCP, while the enthalpies of the phases are comparable, which causes the former to be lower in free energy. By increasing the confinement height, the phase switches to be 6L-BCC. This transition is governed by the entropy since the entropy of the 5-layers phases shoots down to that of BCC (red line in Figure 4.4b)), while the enthalpies gradually increase. The further confinement height increase causes the transition from 6L-BCC to 6L-FCC. Decomposing the free energy can show a clearer picture of the behaviour. The enthalpies of the phases gradually increase while the entropy contribution of

BCC becomes smaller compared with that of FCC and HCP at the confinement height $h \approx 7.4$ where the transition occurs.

Comparison with experiments

We, now, compare the phases found in our simulation with the experiment. In Figure 4.5, the top panel are the snapshots from the experiments and the bottom panel are the snapshots from the simulations. For the simulation, we did not show the 1-layer phase since it is similar to that of the experiment, Figure 4.5 top panel A. Instead, we show the phase that we found in the simulation which does not exist in the experiment which is BCC, Figure 4.5 bottom panel D. The rest of the phases exist in both simulations and experiments are matched. The snapshots in Figure 4.5 both top and bottom panels show a series of reentrant behaviour of BCC-FCC phase with rhombic phase in between as a metastable phase at confinement height $h \leq 4\sigma$. We also plot the two-dimensional radial distribution function of the layer parallel to the confining wall as shown in Figure 4.6. The radial distribution function from simulations mostly matches with the one from experiments. Also, one can clearly see the reentrant behaviour between BCC-FCC with the variation of the confinement height, variation from the notched second peak which is the signature of the hexagonal plane to a single second peak which represents the square pattern and so forth.

In Figure 4.7, we plot the phase diagram in interlayer distance $D = h/N_L$ and number of layers N_L . The results from simulation match well with the result from the experiments. As the layer number increases, the range of interlayer distance becomes narrower. At $N_L < 11$, larger D induces the FCC phase while smaller D induces the BCC phase. When $N_L > 14$, the FCC phase becomes fewer and the phase behaviour of the bulk BCC-stable regime is recovered. Lastly, we also find that as the confinement height increases, e.g. at $N_L = 11$ as shown in Figure 4.8, the rhombus angle decreases from $\theta \approx 72^\circ$ of BCC phase to below $\theta < 65^\circ$ which is the rhombus angle of FCC(111) structure. In the same figure, we also plot the change in the rhombus angle along with the change in b/a ratio, ratio between long and short diagonal lines of the rhombus, and one can clearly see the distortion of the lattices initially from BCC(110) lattice, $b/a = \sqrt{2}$, toward the final

FIGURE 4.5: Snapshots of the system in BCC-stable system. (Top panel) the snapshots from experiments at difference confinement heights. (Bottom panel) the snapshots from simulations at difference confinement heights. N_L represents the number of layer of the crystal. Rhombic, FCC(111) and BCC(110) are determined by the angle of the particles alignment.

FIGURE 4.6: Two dimensional radius distribution function, $g(r)_{2D}$, of the phases show in Fig.4.5. The solid lines are the results from experiments and the dash lines are the results from simulations.

FIGURE 4.7: Phase diagram in the interlayer distance $D = h/N_L$ and the number of layer N_L . The open symbols represent data points obtained from simulations and the solid symbols represent data points obtained from experiments.

FCC(111) lattice, $b/a = \sqrt{3}$, as the interlayer distance D increases. This example can illustrate the transition from BCC to FCC.

FIGURE 4.8: Illustration of distortions of the lattices. (As increasing of the interlayer distance D at $N_L = 11$, we observe a corresponding decreasing of the rhombus angle. Below 65° , the structure changes to a fcc-type. b/a is the ratio between long and short diagonal line of the rhombus. BCC(110) has $b/a = 1.41$ and FCC(111) has $b/a = 1.73$. The open symbols represent data points and dash lines obtained from simulations and the solid symbols and solid lines represent data points obtained from experiments.

Conclusions

In this chapter, we systematically studied the phase behaviour of the repulsive Yukawa colloidal system confined between two flatted walls in the parameter regime where the BCC lattice is the stable phase in the bulk system. We found the FCC-BCC reentrant behaviour which is different from the confined hard-sphere system. Free energy calculation reveals that this reentrant behaviour is governed by the entropy and can go up to 14 layers where the FCC phase becomes rare. By comparing with the experimental results, we found the consistency in between the simulation and experiments which can shed light on the bottom-up approach for the fabrication of micro- or macroscale colloidal crystal films with highly complicated nanostructures to provide cheaper and scalable processes that are highly beneficial for industrial applications.

Chapter 5

Vacancy removal via perturbing curved wall

Introduction

Solids at a given finite temperature always contain defects. They can be categorized into three types: point defects, line defects and planar defects. These defects considerably contribute in the mechanical and transport properties of crystals, e.g. mechanical instabilities such as creep, yield, and fracture or thermal conductivity [94,95]. The simplest kind of defect is vacancy which belongs to the point defect class. This type of defect refers to the missing of an atom or atoms from the lattice sites and generally be formed during solidification process owing to vibration or local rearrangement of atoms.

In hard sphere system, the equilibrium concentration of monovacancies is found to be high close to the melting point with the mole fraction $\approx 10^{-4}$ i.e. one vacancy per 10,000 lattice sites. This concentration is higher than that of di-vacancies, $\approx 10^{-9}$, and Tri-vacancies, $\ll 10^{-10}$ [96]. A vacancy moves via substitutional diffusion. In this process, the adjacent atom will hop into the vacancy site and create a vacancy on its previous site. This mechanism has been found to be temperature dependent and governed by enthalpy [97]. The interaction between vacancies are found to be weakly attractive and short-ranged, only the neighbouring lattice can be affected [98]. For softer systems, e.g. dipolar spheres, the study shows that in 2D colloidal crystals the interaction between both vacancies and interstitials are strongly attractive [99]. The range of interaction is around 6-7 lattice spacings for both interstitial-interstitial (I-I) and vacancy-vacancy (V-V). Furthermore, if

multiple vacancies or interstitials exist in the system they tend to form defect clusters.

Since defects are highly dynamic compared to the static background crystals and hop from sites to sites by diffusion. Here in this chapter, we implement the fact that vacancies interact with each other to propose a novel path to eliminate vacancies in a crystal phase by perturbing the background crystal phase by a curved wall to create the disorder region at the wall surface which can act as a pool of defects at the outskirts of the crystal. By adopting this concept, we simulate a dipolar colloidal system confined between two walls, flat wall and curved wall, contains vacancies and study their dynamics. The results show that when vacancies approach the curved wall, they merge and stay at the surface of the curved-wall throughout the simulation.

Methodology

Model

The system we study consists of N particles in two dimensions where inter-particle interaction can be described as the pair potential:

$$\beta v(r) = \frac{3^{3/4}\Gamma}{(2\pi)^{3/2}} \left(\frac{a}{r}\right)^3 \quad (5.1)$$

where Γ is the coupling parameter which can be interpreted as an inverse temperature, a is lattice spacing of a perfect hexagonal lattice with density $\rho = 2/(\sqrt{3}a^2)$. Such an interaction can be realized with superparamagnetic colloidal particles dispersed in a flat air-water interface and exposed to a magnetic field B perpendicular to the interface [100]. The particles are confined in y -direction with in two walls, a flat wall and a curved wall as shown in Figure 5.1. The purpose of confining the system with the curved wall is to introduce perturbation to the crystal phase to create a "disordered" region close to the crystal-curved wall interface.

In order to determine the overlap between a particle and the curved wall, we adopted the algorithm proposed in ref. [101]. The general expression for an ellipse in polynomial and parametric form are

$$\frac{x^2}{A^2} + \frac{y^2}{B^2} = 1 \quad (5.2)$$

where A and B are the semi-axis length along the x-axis and the semi-axis length along the y-axis respectively. In general case, the ellipse can be rotated and translated from the origin by amount $(-h, -k)$ and then rotated through an angle $-\varphi$ and these translations can be written in a matrix form as:

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos(-\varphi) & -\sin(-\varphi) \\ \sin(-\varphi) & \cos(-\varphi) \end{bmatrix} \cdot \left\{ \begin{bmatrix} x \\ y \end{bmatrix} + \begin{bmatrix} -h \\ -k \end{bmatrix} \right\} \quad (5.3)$$

This equation can be rearranged to the form of Eq.5.2 as:

$$\frac{[\cos(\varphi) \cdot (x - h) + \sin(\varphi) \cdot (y - k)]^2}{A^2} + \frac{[-\sin(\varphi) \cdot (x - h) + \cos(\varphi) \cdot (y - k)]^2}{B^2} = 1 \quad (5.4)$$

Alternatively, one can expand Eq.5.4 and write in the form:

$$a_{1,1} \cdot x^2 + 2 \cdot a_{1,2} \cdot x \cdot y + a_{2,2} \cdot y^2 + 2 \cdot a_{1,3} \cdot x + 2 \cdot a_{2,3} \cdot y + a_{3,3} = 0 \quad (5.5)$$

or in matrix equation $X^T \cdot A \cdot X = 0$ as:

$$\begin{bmatrix} x & y & 1 \end{bmatrix} \cdot \begin{bmatrix} a_{1,1} & a_{1,2} & a_{1,3} \\ a_{1,2} & a_{2,2} & a_{2,3} \\ a_{1,3} & a_{2,3} & a_{3,3} \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ 1 \end{bmatrix} = 0 \quad (5.6)$$

FIGURE 5.1: Illustration of N particles with diameter σ confined, in y -direction, between parallel hard wall and curved wall. The curved wall is defined as a half-ellipse with semi-major and semi-minor axes length A and B respectively. The dot grid line is the perfect hexagonal lattice used to locate the vacancy. The periodic boundary condition in x -direction is applied. The unfilled green circle marks the location of the vacancy.

For two ellipses with coefficient matrices $A = [(a_{i,j})]$ and $B = [(b_{i,j})]$, the characteristic polynomial is:

$$f(\lambda) = \det(\lambda \cdot A + B) = \lambda^3 + a \cdot \lambda^2 + b \cdot \lambda + c \quad (5.7)$$

where a, b and c is coefficients whose its expression can be found in ref. [101]. It has been proven that two ellipses A and B are separated only if $f(\lambda)$ has two distinct positive real roots and one negative real root [102]:

$$\begin{aligned} a \geq 0, \quad -3b + a^2 > 0, \quad 3ac + ba^2 - 4b^2 < 0, \\ -27c^2 + 18cab + a^2b^2 - 4a^3c - 4b^3 > 0 \end{aligned} \quad (5.8)$$

$$a < 0, \quad -3b + a^2 > 0, \quad -27c^2 + 18cab + a^2b^2 - 4a^3c - 4b^2 > 0 \quad (5.9)$$

We study the trajectory of the a vacancy using Monte Carlo simulations in the NVT ensemble with periodic boundary conditions applied to the x-direction of the simulation box, for the case of 2D system, and in x- and z-directions, in case of 3D. To determine the location of the vacancy, we introduce a background perfect hexagonal lattice consisting of $n = N$ lattice sites. Each particles is assigned to the nearest lattice site. Thus, each lattice site can have either zero or one particle assigned to it, the lattice sites with zero particle is identified as a vacancy site.

The simulations start with the perfect 2D hexagonal crystal, each particle sits at a site of the perfect lattice. After equilibrating the system, a particle is removed from the crystal to create a vacancy site. During the Monte Carlo simulation, the crystal slowly diffuses from its original configuration. Thus, the underlying lattice must be intervally adjusted to synchronize the diffused crystal. This can be done by shifting the underlying lattice with the average distance in x- and y-direction from their assigned particles every MC step.

Results

2D: Vacancy trajectory and probability

For 2D case, we first study the diffusion of a vacancy by using the method stated in the methodology section. The location of the vacancy is tracked throughout the simulation time and plotted as shown in Figure 5.2.

Starting from the bottom of the lattice, close to the flat-wall, the vacancy travels throughout the phase space and eventually merges with the disordered region around the curved-wall surface. To illustrate this merging event, we plot the average probability of finding the vacancy as a function of y as shown in Figure 5.3 (c). As one can clearly see from the plot that there is a sharp peak around $y \approx 16\sigma$ which is the location of the curved-wall, where the small peaks at small y corresponds to those movements around the bottom of the lattice at the beginning of the simulation, in agreement with Figure 5.3 (a). By further increasing the simulation time, we show that the probability peak around the curved-wall surface becomes sharper and the trajectory plot shows that for two thirds of the simulation time,

FIGURE 5.2: The trajectory of the vacancy from the system with $N = 400$ particles at $\eta = 0.5$, $\Gamma = 120$ and $wall_{rad} = 3.5\sigma$ mapped with the hexagonal lattice on the background. The colorbar on the right shows the propagation of the simulation time.

the vacancy stays at the curved-wall surface after the merging, Figure 5.3 (d) and (b) respectively.

We, now, turn our focus to study the system size dependence by increase the size of the system from $N = 400$ to $N = 900$, $N = 1600$ and $N = 2500$.

The plots illustrate in Figure 5.4 show both trajectory and probability of finding the vacancy projected on y-direction for different system sizes. For the system size of $N = 400, 900$ and 1600 , the trajectories with the simulation time $480M$ MCs step show the merging of the vacancy with the disordered-phase at the curved-wall surface where its locations show the highest peak of the probability plot. Only for the case of system size $N = 2500$ which the simulation time $480M$ MCs is not enough for the vacancy to travel to the curved-wall, the green line in Figure 5.4d). By increasing the simulation time to $960M$ and $1200M$ MCs, red and blue lines in Figure 5.4d) respectively, the vacancy is ultimately merged with the disordered phase. By plotting the probability,, one can clearly see the shifting of the peak from left to right owing to the increase of the simulation time.

FIGURE 5.3: (Top panels) The trajectory plot on xy-plan and (Bottom panels) the probability plot in y-direction of the vacancy from the system with $N = 400$ particles at $\eta = 0.5$, $\Gamma = 120$ and $wall_{rad} = 3.5\sigma$ with simulation time a,c) 240m MC steps and b,d) 480m MC step. The colorbar on the right shows the propagation of the simulation time.

2D: Vacancy starting point dependence

To study effect of the vacancy starting point, we vary the deleted particle location from 75th to 23rd, 46th, 52nd and 102nd, the 1st particle locates at the very left bottom corner of the simulation box, and plot the probability as function of position in the y-direction as shown in Figure 5.5. As one can clearly see from the plot, the probability has the highest peak for all cases around $y \approx 16\sigma$ which is the location of the curved-wall. Also, the height of the peaks which can be interpreted as the time that the vacancy spends in that region for each case is qualitatively comparable. Thus, one can conclude that the starting point is not correlated with the mobilizing behaviour of the vacancy inside the crystal, the vacancy eventually merges to the phase at the surface of the curved-wall and if the simulation time is long enough the height of the peak will be eventually equal for all the cases.

FIGURE 5.4: (Top panels) Trajectory of the vacancy and (bottom panels) probability of finding the vacancy projected on y-direction of system with size $N =$ a,d) 400, b,e) 900, c,f) 1600 and d,g) 2500 particles. The colorbars in top panels represent the propagation time of the MC step

FIGURE 5.5: Probability plot of the system with a vacancy started from different positions.

2D:Curvature dependency

In this section we study the curvature of the curved-wall effect on the behaviour of the vacancy. The plot in Figure 5.6a) shows the probability of finding the vacancy of

FIGURE 5.6: a) Probability of finding the vacancy with different curvatures. b) The trajectory of the vacancy with the curvature of 2.0σ c) The snapshot of the simulation with the curvature of 2.0σ . d) The snapshot of the simulation with the curvature of 2.5σ . In c) and d), the area enclosed in the dash circle is the disorder region due to the present of the curved-wall.

the system with different curvatures, from 2.0σ to 5.5σ . As the curvature increases, the location of the probability peak is shifted to the left handside which refers to the shifting of the position of the surface of curved-wall downwards in y-direction. The highest peak is from the 4.5σ case which refers to the fastest time for the vacancy to travel and merge with the phase at the surface of the curved-wall. Only in the case of curvature 2.0σ that the vacancy seems to stuck at the middle of the simulation box, the small red peak at $y \approx 17\sigma$ in Figure 5.6a). When we plot the trajectory of the vacancy as shown in Figure 5.6b) we can clearly see that the vacancy is stuck at the middle of the simulation box, Figure 5.6c). Just to compare the range of the affected area from the curved-wall with the case of the curvature 2.5σ , Figure 5.6d), one can observe that the range of the area in the dash circle from the curved-wall of the 2.0σ is longer than 2.5σ case which can state that the smaller curvature, the longer affected range in the crystal phase.

2D:two vacancies

FIGURE 5.7: (Top) Trajectories of two vacancies started from 30 and 100, a), and 10 and 109, b). The left color bar represent the propagation time of the simulation of 30th and 10th vacancy while the left one represent the 100th and 109th. (Bottom) Probability of finding the vacancies which started from 30 and 100, c), and 10 and 109, d).

Now, we increase the number of vacancies in the system to two and trace their behaviour. The two vacancies are initially located at different locations, 30/100 and 10/109. In Figure 5.7 the top panel illustrates the trajectories of the two vacancies with different starting points. Both cases show that shortly after the simulation starts, no matter how far the vacancies be apart from each other, they will merge and travel through out the phase space and eventually merge with the perturbed phase at the surface of the curved wall, as shown by Figure 5.7a) and c). By plotting the probability of finding the vacancies, we can clearly see that the distributions of the two vacancies are mostly overlapped with each other indicating that the two vacancies are initially merged and diffuse together. One observation is that in the case of 10/109, the vacancies merge at the very first stage of the simulation and travel to the curved wall while in the 30/100 case the vacancies initially mount

for a short time and then unmount and travel to the curved wall independently and eventually mount again at the wall. The travelling time of the two cases are reflected as the height of the distribution peak, the early case shows the slower diffusion compared to the later case. Thus, one can preliminary state that if two vacancies merge and stick together throughout the simulation, the diffusion of this pair toward the curved wall is faster than the single vacancy diffusion. This finding is consistent with the results in Lennard-Jones systems where the two-point vacancy has a much higher mobility than the one-point vacancy due to the extra voids around the dimer which boost up the activity of motion and facilitates the diffusion [103].

2D:Mean square displacement and diffusivity as function of packing fraction

FIGURE 5.8: a) Mean square displacement and b) diffusion coefficient of the vacancy in systems comprised of $N = 400$ particles.

By measuring the mean square displacement which is defined as:

$$MSD \equiv \langle (r - r_0)^2 \rangle \quad (5.10)$$

where x_0 is the original position of the vacancy at the beginning of the simulation. The plot in Figure 5.8a) shows that by increasing the density of the solid phase,

the mobility of the vacancy becomes more difficult and the vacancy gets stuck at its original position or simply fluctuates around when $\eta \geq 0.51$. Also in the regime that $0.48 \leq \eta < 0.51$, increasing the packing fraction of the crystal slows down the mobility of the vacancy toward the curved-wall as one can observe from shifting of the jump of the MSD to the plateau which refers to the position on the surface of the curved-wall to right handside of the case $\eta = 0.48$ to $\eta = 0.50$, blue, purple and black lines in Figure 5.8a). We further examine the diffusion of the vacancy by calculating the diffusion constant from the mean square displacement as:

$$D = \lim_{t \rightarrow \infty} \frac{\langle \Delta r^2(t) \rangle}{4t} \quad (5.11)$$

We plot the diffusion coefficient for the vacancy as shown in Figure 5.8b). The diffusion slows down rapidly with increasing the packing fraction. This can be explained as once the vacancy diffuses, a neighbouring particle hops into it which becomes more difficult as the density increases.

3D

FIGURE 5.9: a) Trajectory of the vacancy b) Probability of finding the vacancy projected in y-direction of the system with packing fraction $\eta = 0.58$.

FIGURE 5.10: (Top) a) Trajectory of the vacancy b) Probability of finding the vacancy projected in y-direction of the FCC crystal with packing fraction $\eta = 0.59$. (Bottom) c) Trajectory of the vacancy d) Probability of finding the vacancy projected in y-direction of the system with packing fraction HCP crystal with packing fraction $\eta = 0.59$. The colorbar in a) and c) represents the propagation of the MC step.

Now, we increase the dimensionality of the system to 3D. By extending the method stated above along with applying periodic boundary condition in z-direction, we can simulate the bulk system. In Figure 5.9a), a typical trajectory of the vacancy is illustrated. One can clearly see that the vacancy diffuses throughout the crystalline lattice and eventually merges with the phase at the surface of the curved-wall, locates at $y \approx 16.5\sigma$. By plotting the probability of finding the defect projected on the y-direction, in x- and z-direction the periodic boundary conditions applied, we can clearly observe the sharp peak at the curved-wall which implies

to the merge of the vacancy with the phase on the surface of the curved-wall, in Figure 5.9b). One problem we observed here is after the vacancy mounts at the surface of the curved wall, it, somehow, unmounts for a short while and diffuses to the center of the crystal and then diffuses back and merges again at the curved wall. We suspect that this is due to the packing fraction of the crystal is a bit too low and, therefore, there is some free volume available for the vacancy to travel to after the merging. Thus, we increase the packing fraction from $\eta = 0.58$ to $\eta = 0.59$ and plot both trajectory and probability distribution as shown in Figure 5.10 (top panel). Here we can see that the probability distribution at $y \approx 15\sigma$ where is the location of the curved wall is higher. This indicates that the vacancy spends more time in this region and the trajectory shows that there is no evidence of dismount of the vacancy from the region at the surface of the curved wall. Yet, one can still observe that the vacancy, however, spends some time in the region close to the flat wall. We suspect that this behaviour is caused by the configuration of the FCC phase that leaves some spaces around the wall due to the stacking in *ABCABC* sequence. When the crystal is equilibrated, the C layer which is shifted in the y-direction from A layer $1/\sqrt{3}$, moves to fill up this space and thus unexpectedly creates cavities around the flat wall. To surmount this issue we replace the crystal with the HCP crystal with the stacking sequence *ABAB*. The corresponding trajectory and the probability plot are shown in Figure 5.10 (bottom panel). As one can realize that the peak of the probability is higher around the curved wall and flatter at the flat wall which refer to the time that the vacancy spends around the curved wall is larger than the one at the flat wall surface.

Conclusion

In summary, we study correlation between vacancies and the disordered region induced by a curved wall in magnetic dipoles systems confined between a flat wall and a curved wall in Both 2D and 3D. We set the system's parameters in the range where a stable hexagonal crystal exists. In 2D case, we illustrate the trajectory of a vacancy that travels throughout the phase space and eventually merges with the disorder region at the surface of the curved wall without detachment. System size dependence studies suggest that increasing the system size only increases the diffusion time of the vacancy toward the curved wall. Furthermore, once we vary the

starting point from where the vacancy diffuses from, the results show no differences of each case which indicates the uncorrelation to the mobility of the vacancy in the crystal phase. By diversifying the curvature of the curved wall between 2.0σ to 5.0σ , the merge region shifted to the lower position in y direction and the curvature 4.5σ leads to the fastest diffusion of the vacancy to the curved wall. At curvature 2.0σ , a cavity is induced by the curved wall arises at the middle of the crystal phase and the vacancy is stuck at the cavity. Thus, the smaller curvature induces the longer affected area, disordered phase, in the crystal phase. Adding another vacancy to the system shows that the monomers bind to each other and the resulting dimer diffuses towards the curved wall. Also, increasing the packing fraction of the host crystal causes the slowing down of the vacancy mobility. The vacancy completely gets stuck at its initial position when the packing fraction reaches $\eta \approx 0.52$. For the 3D case, the vacancy also diffuses towards the curved wall and merges. The detachment can be observed in the 3D case where the crystal phase stacks in the form of ABCABC. The crystal exhibits the shift of the C layer in y -direction to facilitate the void created by the curved wall. This causes the cavities left at the other end, at the surface of the flatted wall. On the other hand, the HCP crystal in which the stack is in the form of ABAB can surmount the issue of detachment. This provides the novel method to disrupt vacancies that formed inside crystal phases which leads the better transport properties for both electron and phonon that causes the better in thermal conductivity of the material.

Chapter 6

Conclusions

The aim of this thesis is to provide an in-depth understanding of system of soft colloids in topographical confinement and their phase behaviour. For that purpose, we employ numerical techniques, specifically Monte Carlo simulations, to simulate colloidal systems in both two- and three-dimensions.

Colloidal systems in confinement exhibit richer phase behaviours compared to their three-dimensional bulk systems. For instance in hard-sphere systems, the confinement promotes a phase transition sequence of $\dots n\Delta \rightarrow (n+1)\square \rightarrow (n+1)\Delta \dots$, where n is the number of crystal layers, apart from the FCC phase in the bulk system. Furthermore, by making the colloidal particles softer, e.g. introducing charges on the colloids, one can expect even richer phase behaviours. In Chapter 2, we investigate the self-assembly of oppositely charged colloids confined between two parallel hard walls. We report a novel phase of multi-layer simple cubic crystals. The stability of this phase increases with decreasing of the inverse screening length, κ . At $k = 3\sigma^{-1}$, at low temperature, we find that this phase can stack up to 4 layers. The free energy calculation reveals that the phase is stabilized against the most energetically favoured close-packed crystals by large vibrational entropy. The further photonic properties calculation of the inverse 4-layer NaCl-like crystal shows the ability of reproducing the large photonic band gaps of the bulk simple cubic crystal which open at low frequency range with low dielectric contrast. This paves novel possibilities of using confined colloidal systems to fabricate open crystalline materials with novel photonic properties.

We further investigate the nucleation of this novel multi-layer simple cubic crystal by implementing umbrella sampling Monte Carlo method (Chapter3). We calculate Gibbs free-energy barriers in supersaturation range $0.33 \leq \beta|\delta\mu| \leq 0.47$ and fit the results with the classical nucleation theory (CNT). We find that the CNT with assuming cylindrical shapes of the nucleus provides a better fit compared to the CNT with spherical nucleus shape. This is the result from the difference in their surface terms wherein the cylindrical surface term the confinement parameter is included. This highlights the effect of the boundaries on nucleation processes.

In Chapter4, we report simulation and experimental results of confined like-charge repulsive systems. The suspension is confined in a wedge with hard flat walls. The colloidal particles here are "softer" compared to the hard spheres. In range of parameters where the BCC lattice is the stable phase in the bulk system, we find FCC-BCC reentrance which differ from the confined hard-sphere system. The free energy calculation shows that this reentrance is dictated by the entropy and can be stacked up to 14 layers whereat the FCC phase becomes subtle. This highlights the bottom-up approach for the fabrication of micro- or macroscale colloidal crystal films with highly complicated nanostructures.

Up to this point, we have extensively discussed on the behaviour of various thermodynamically stable phases, mostly on energetic point of view. It is worth discussing on the sensitivity of the key results to the choice of force fields. As shown in chapter 2 and 4, the stability of the simple cubic and FCC-BCC re-entrance are very sensitive to the degree of confinement. With slight modification of confining walls by replacing one of them with an attractive wall, at sufficiently strong attraction, the formation of NaCl phase can be surpassed by the CsCl phase [104]. Furthermore, it has been found that by switching the attractiveness to repulsive one the freezing behaviour is reciprocated, i.e. for attractive walls crystallization arises at the wall surfaces while for repulsive walls the freezing occurs from the middle [105]. Alternatively, if one change the shape of the confining wall from flat to cylindrical in Yukawa systems the re-entrance behaviour can be found as in chapter 4. The difference is in this case one can expect a transition between non-helical and helical structures [106,107] rather than FCC and BCC.

In the last chapter, we show how to utilize the confinement to eradicate vacancies formed in colloidal crystals in magnetic dipoles systems. The crystals are confined between a flat wall and a curved wall. The latter one is introduced to create a

disordered region to trap the existing vacancies. By tracking the trajectory of a single vacancy, we find that the vacancies travel through the phase space and merge with the perturbed region at the surface of the curved wall. The traveling time to the region is system size dependent with no correlation with its initial position. At the curved wall with radius of the curvature 4.5σ , the vacancy can diffuse fastest. In the case of two-vacancies, the monomers bind to each other and diffuse towards the curved wall.

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