

Polymorph selection in the crystallization of hard-core Yukawa system

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Received May 5, 2015; accepted June 8, 2015; published online September 21, 2015

Colloid-colloid interactions in charge-stabilized dispersions can to some extent be represented by the hard-core Yukawa model. The crystallization process and polymorph selection of hard-core Yukawa model are studied by means of smart Monte Carlo simulations in the region of face-centered-cubic (fcc) phase. The contact value of hard-core Yukawa potential and the volume fraction of the colloids are fixed, while the Debye screening length can be varied. In the early stage of the crystallization, the precursors with relatively ordered liquid structure have been observed. Although the crystal structure of thermodynamically stable phase is fcc, the system crystallizes into a mixture of fcc and hexagonal close-packed (hcp) structures under small Debye screening length since the colloidal particles act as effective hard spheres. In the intermediate range of Debye screening length, the system crystallizes into a mixture of fcc, hcp, and body-centered-cubic (bcc). The existence of metastable hcp and bcc structures can be interpreted as a manifestation of the Ostwald's step rule. Until the Debye screening length is large enough, the crystal structure obtained is almost a complete fcc suggesting the system eventually reaches to a thermodynamically stable state.

colloidal crystallization, hard-core Yukawa model, polymorph selection, computer simulation

Citation: Ouyang WZ, Sun ZW, Zhong J, Zhou HW, Xu SH. Polymorph selection in the crystallization of hard-core Yukawa system. *Sci China Chem*, 2016, 59: 316–323, doi: 10.1007/s11426-015-5473-z

1 Introduction

Charge-stabilized colloids have received tremendous attention in the past decades because of their interesting characteristics and complex behaviors [1,2]. As is known, the system with charge-stabilized colloids under appropriate conditions can be self-assembled into highly ordered arrays of particles, i.e. colloidal crystals. Such structural ordering of colloidal particles directly appears analogous to their atomic or molecular counterparts, therefore a useful model system of colloids can be provided to study general principles of the crystallization of materials [3]. Moreover, time and

length scales in colloidal crystals are several orders of magnitude larger than those of atomic or molecular crystals, so one can acquire more suitable tools and instruments for observation and measurement of the crystal growth.

In general, the essential physics of the crystallization can be understood in the framework of the classical nucleation theory, in which the initial homogeneous disordered liquid and final ordered crystal phases are the only key players of nucleation. But the actual crystallization process is not that simple and the mechanism is more subtle than expected. In 1897, Ostwald [4] formulated his step rule, stating that the crystal phase that is nucleated from the melt need not be the one that is thermodynamically most stable, but the one that is closest in free energy to the fluid phase. Alexander and McTague [5] argued, on the basis of Landau theory, nuclea-

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tion of the body-centered-cubic (bcc) phase should uniquely be favored in the early stage of a simple fluid which exhibits a weak first order phase transition. Very recently, our group observed the process of metastable bcc phase transition in charge-stabilized colloidal system [6]. With controversy, some more studies have shown that the present understanding of crystallization is still far from complete and that the story of crystallization does not end yet. ten Wolde *et al.* [7,8] found by numerical simulations of a Lennard-Jones system that the precritical nuclei are predominantly bcc ordered despite the stable structure is face-centered-cubic (fcc) crystal, and the core becomes fcc ordered while its interface retains a high degree of bcc-like ordering as the nucleus grows to its critical size. Desgranges and Delhomme [9] studied the crystallization of silicon via molecular simulation to establish a pivotal role played by liquid polymorphism, which suggests that Ostwald's step rule should be extended to include the role of liquid polymorphism. Furthermore, both experiments and simulations in recent years have given the mounting evidence that the crystallization or nucleation in simple liquids is a two-stage process [10–15]. The first stage involves the formation of amorphous precursors with different types of short-range order, which assists crystal nucleation. Then, in the later stage of the actual crystallization process, the precursors develop into a crystalline phase that is determined by the nature of the interparticle interactions [15]. However, very recent researches have proposed that the nucleation process does not consist of discrete steps but is rather continuous at the microscopic level [16–18]. In other words, the precursors are not completely amorphous, but regions of high bond orientational order, and the development of bond orientational order is continuous [19].

Understanding the mechanisms to gain an insight into the crystal formation of charge-stabilized colloids is of fundamental importance to assess the validity of crystallization theories and to control crystal morphology. Previously Desgranges and Delhomme [20,21] performed molecular dynamics simulations to investigate the polymorph selection during the crystallization of point Yukawa systems. They showed that the crystallization mechanism strongly depends on the value of a screening parameter. In the present study, we will address the homogeneous nucleation of hard-core Yukawa model. This model is also a good approximation for the effective pair interaction between the charge-stabilized colloids. Based on the prediction of the so-called DLVO theory proposed by Derjaguin, Landau, Verwey and Overbeek [22], the effective pair interaction between the charge-stabilized colloidal particles consists of a hard-core repulsion due to the finite size of the colloidal particles and the screened-Coulomb repulsion with the screening length given by the Debye length of the electrolyte, and short-ranged van der Waals attractions. The Debye screening length, which defines the thickness of the double layer of opposite charge surrounding each colloidal surface, is not a

constant but does depend on the thermodynamic state of the system. In most situations except a very short distance the van der Waals attractions can be neglected, so one may assume simply that the interaction between charged colloids is approximately represented by a hard-core Yukawa potential.

Polymorphism is the ability for a component to crystallize in different structures. Since each polymorph has specific properties, it is crucial for the charged colloids to control which crystal structures can form during a nucleation event. So, this raises the issue of a complete understanding when or how the crystal polymorph will be formed during the crystallization process, although computational, theoretical, and experimental investigations so far have constructed the phase diagram and shown some relevant crystallization observations [6,18,23–27]. Especially, the underlying selection mechanism of the crystal polymorph still remains elusive, even as the stable crystal structure is known to be dependent on the interactions and the volume fraction of colloids.

Here we apply the method of smart Monte Carlo (SMC) [28,29], which is expected to be more efficient and produce more rapid convergence than the standard Metropolis method, to investigate the crystallization process of hard-core Yukawa model. Taking into account many-body effects in concentrated charge-stabilized suspensions, the effective colloid-colloid pair interaction resembles closely a truncated hard-core Yukawa potential [30]. As the corresponding phase diagram has already been determined in previous work [31], we will take advantage of the phase diagram to study the local packing symmetry and the relevant pathway for crystallization. The simulations are carried out in the region where fcc crystal structure should be thermodynamically stable. We only vary the Debye screening length and fix other parameters of charged colloids, to observe the polymorph selection in the crystallization process. We show that the structures of the crystal formed in charged colloids strongly depend on the Debye screening length. Our results may be helpful to further understanding of both colloidal crystallization and its subtle mechanism.

2 Model and simulation methodology

The charge-stabilized colloidal particles are approximately interacted by a truncated hard-core Yukawa potential, which is defined by:

$$\beta U(r_{ij}) = \begin{cases} \frac{\beta \varepsilon}{r_{ij}} \exp[-\kappa(r_{ij} - d)], & r > d \\ \infty, & r \leq d \end{cases} \quad (1)$$

where r_{ij} is the pair distance between i th particle and j th particle. The parameter ε governs the strength of the interaction, κ is the inverse Debye screening length, and d is the

hard-core diameter of colloidal particles. The parameter $\beta = 1/k_B T$, where k_B is the Boltzmann constant and T is the temperature of the system. For convenience, the reduced units are used in the simulations. The basic units are chosen as follows: energy units $k_B T$; the mass of colloidal particles m ; the relevant length scale $L_0 = (6V/\pi N)^{1/3}$, where N is the number of particles and V is the volume of simulation box. So, $d = \phi^{1/3}$ in reduced units, where ϕ is the volume fraction of colloidal particles. In the limit of very short-range and weak repulsions, where $\varepsilon \rightarrow 0$ and $\kappa \rightarrow 0$, the hard-core Yukawa potential reduces to hard-sphere potential.

For the SMC simulation, the tentative trajectories are generated using the Ermak algorithm [32]:

$$\Delta \vec{r}_i = \beta D \vec{f}_i \Delta t + \vec{r}_i^G \quad (2)$$

where $\Delta \vec{r}_i$ is the displacement in a time step Δt , \vec{f}_i is the force on the particle at the beginning of the step, D is the diffusion constant in the absence of interparticle interactions, and \vec{r}_i^G is the random displacement which is chosen independently from a Gaussian distribution with zero mean and variance $\langle (r_{i\alpha}^G)^2 \rangle = 2D\Delta t$ ($\alpha = x, y, z$). We set for simplicity $A = D\Delta t$ as a single adjustable parameter, so Eq. (2) becomes simply:

$$\Delta \vec{r}_i = \beta A \vec{f}_i + \vec{r}_i^G \quad (3)$$

In a typical SMC move, the trial displacement of the particle is according to Eq. (3), and the move is accepted with probability $\min(1, P_{\text{SMC}})$. P_{SMC} is calculated via [28,29]

$$P_{\text{SMC}} = \exp\{-\beta[\Delta U + \frac{1}{2}(\vec{f}_i + \vec{f}_i^{\text{new}}) \cdot \Delta \vec{r}_i + \Delta W_{\text{SMC}}]\} \quad (4)$$

where

$$\Delta W_{\text{SMC}} = \frac{\beta A}{4} (\vec{f}_i^{\text{new}} + \vec{f}_i) \cdot (\vec{f}_i^{\text{new}} - \vec{f}_i) \quad (5)$$

ΔU is the potential difference between new state and old state, and \vec{f}_i^{new} is the force on the particle in new state. In fact, SMC simulations with N -particle moves and small step sizes are almost identical with Brownian Dynamics (BD) simulations, besides the extra flexibility lies in the possibility of using larger step sizes and in being able to move any number of particles from 1 to N . Notice that here only one particle is moved in a step of SMC simulation in order to get a larger step size and higher acceptance ratio of the trial moves.

In the nucleation process, it is needed to be able to distinguish particles that are part of the crystal from those that belong to the liquid. We use the method presented by Frenkel and co-workers [8]. In this method, the type of the particle is determined based on its local environment. First, the complex vector $q_{lm}(i)$ of particle i is defined as:

$$q_{lm}(i) = \frac{1}{N_{nb}(i)} \sum_{j=1}^{N_{nb}(i)} Y_{lm}(\vec{r}_{ij}) \quad (6)$$

Here $N_{nb}(i)$ is the number of nearest neighbors of particle i . The functions $Y_{lm}(\vec{r}_{ij})$ are the spherical harmonics, l is a free integer parameter and m is an integer that runs from $m=-l$ to $m=l$. Using the complex vectors $q_{6m}(i)$, a scalar product which measures the correlation between neighboring particles i and j can then be defined by:

$$S_{ij} = \sum_{m=-6}^6 d_{6m}(i) \cdot d_{6m}^*(j) \quad (7)$$

where the superscript * indicates complex conjugation. Notice that $q_{6m}(i)$ should be normalized:

$$d_{6m}(i) = \frac{q_{6m}(i)}{\left(\sum_{m=-6}^6 |q_{6m}(i)|^2\right)^{1/2}} \quad (8)$$

Two neighboring particles i and j are defined to be connected if the scalar product S_{ij} described above exceeds a given value, typically $S_{ij} > 0.7$. A particle will be identified as solid-like if the number of connections is above a certain threshold, typically 8.

In order to further assert the structural identity of each crystal particle, we use the averaged bond order parameters introduced by Lechner and Dellago [33]. Different from Eq. (6), the averaged complex vector $\bar{q}_{lm}(i)$ of particle i is defined as:

$$\bar{q}_{lm}(i) = \frac{1}{N_{nb}(i)} \sum_{k=0}^{N_{nb}(i)} q_{lm}(k) \quad (9)$$

Here the sum from $k=0$ to $N_{nb}(i)$ runs over all neighbors of particle i plus the particle i itself. Given the definition of $\bar{q}_{lm}(i)$, one can construct the bond order parameters of averaged version:

$$Q_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |\bar{q}_{lm}(i)|^2} \quad (10)$$

and

$$W_l(i) = \sum_{m_1+m_2+m_3=0} \begin{pmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{pmatrix} \frac{\bar{q}_{lm_1}(i) \bar{q}_{lm_2}(i) \bar{q}_{lm_3}(i)}{\left(\sum_{m=-l}^l |\bar{q}_{lm}(i)|^2\right)^{3/2}} \quad (11)$$

where the term in parentheses is the Wigner $3j$ symbol. The integers m_1 , m_2 , and m_3 run from $-l$ to l , but only combinations with $m_1+m_2+m_3=0$ are allowed. To further identify the solid-like particles, we take advantage of the different symmetries that the crystals have on the W_6 and W_4 axis [34]. We use the following criterion for crystal classification: first, crystal or solid-like particles are identified using

the method presented by Frenkel and coworkers which has been described above. Then, we identify (i) fcc particles as all crystal particles with $W_6 < 0$ and $W_4 < 0$; (ii) hcp particles as all crystal particles with $W_6 < 0$ and $W_4 > 0$; (iii) bcc particles as all crystal particles with $W_6 > 0$.

The simulations are performed in canonical (NVT) ensemble. The periodic boundary condition is applied. The simple truncation of interactions and the minimum image convention are used [35,36], where the cutoff distance is chosen as $r_{\text{cut}}=1.9$ in reduced units. The maximum displacement of the particles is chosen so that about half the trial moves are accepted. A Monte Carlo sweep (MCS) is defined as the set of N configurations during which, on average, each particle gets a chance to move. Initially we place the particles randomly in a three-dimensional cubic simulation box. After a long enough period of MCS, typically 1.9×10^6 MCS, the system can reach equilibrium and some parameters of the properties are calculated during another long runs, typically 10^5 MCS, in order for accurate value obtained.

3 Results and discussion

We fix the contact value of hard-core Yukawa potential as $\beta\varepsilon=81$, which is the same as that in Ref. [31]. The Debye screening length $1/\kappa d$ can be tuned. The number of colloidal particles in the simulations is kept as $N=4000$. The volume fraction of the colloidal particles is taken as $\phi=0.3$, so that the system can have a large region of stable fcc phase. Notice here that the cutoff distance $r_{\text{cut}}=1.9$ used is slightly larger than that in Ref. [31], so there is a little difference of the fcc phase region correspondingly. As is expected, the system exhibits a re-entrance of the fluid phase: one may observe a sequence of fluid, fcc and again a fluid phase with the increasing of $1/\kappa d$. In this paper, we mainly focus on the crystallization in the region of fcc phase.

Firstly we concentrate on the crystallization of the system at lower value of Debye screening length $1/\kappa d=0.1$. Here the degree of crystallinity f_{crystal} is defined as the number of particles in solid-like environments divided by the total number of particles N . In the top of Figure 1, the evolution of f_{crystal} during the crystallization is displayed. Obviously the simulation is started from a random configuration at which $f_{\text{crystal}} \approx 0$, i.e., the system is initially in a liquid state. As the system begins to crystallize, more and more colloidal particles become solid-like so that the value of f_{crystal} increases apparently. Eventually the system crystallizes completely after about 6×10^5 MCS. The averaged RDF curve of the system calculated after the equilibrium (Figure 1) shows that the first peak is at the pair distance $r=0.88$ which is close to the nearest interparticle separation of both bcc lattice and fcc lattice. And the first minimum of the RDF curve is near the pair distance $r=1.1$, so we take $r_{\text{nb}}=1.1$, i.e., two particles will be considered to be neighbors

if their distance is less than $r_{\text{nb}}=1.1$.

Using Eqs. (9) and (11), we can calculate the bond order parameters to further analyze the crystal structure of the solid-like particles. Seen from Figure 2, the number of fcc and bcc particles firstly reach maximum at about 5×10^5 MCS and then decrease while the number of hcp particles always increases before the crystallization is completed. This means that some of fcc and bcc particles have probably transformed into hcp particles in the late stage of crystallization. When the system achieves an equilibrium, it crystallizes into a mixture of fcc and hcp particles while there is very few bcc particles (see the final configuration inside the top panel of Figure 1). This observation is exactly close to

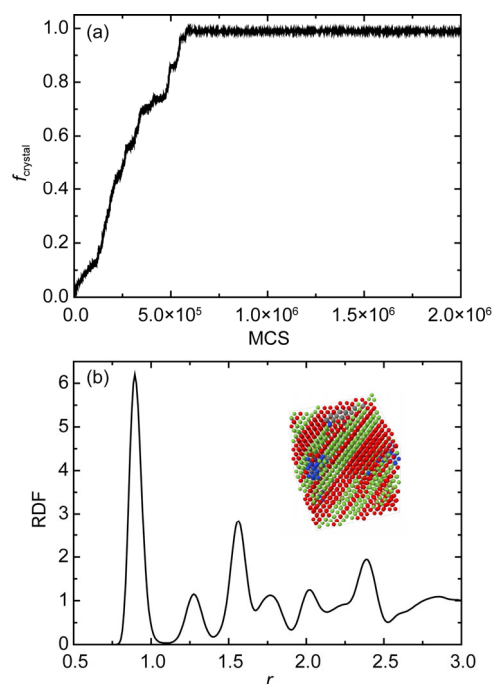


Figure 1 (a) The evolution of the crystallinity during a SMC simulation; (b) the curve of averaged RDF after the system's equilibrium, and the inside is the final configuration of the crystallization (red, green and blue spheres represent fcc, hcp and bcc particles, respectively). The Debye screening length $1/\kappa d=0.1$. (color online)

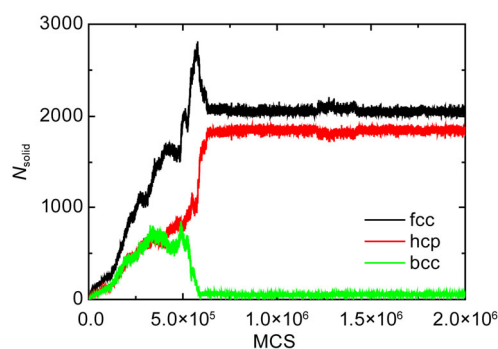


Figure 2 The number of solid (fcc, hcp, and bcc) particles evolves during a SMC simulation when $1/\kappa d=0.1$. (color online)

the phenomenon happened to the hard-sphere system, which has been confirmed by both experiments and computer simulations [37,38]. In the case of hard spheres, it is already known that fcc is the thermodynamically stable crystal structure, but the free energy difference between fcc and hcp is very small resulting in the nucleation of a random mixture of fcc and hcp structure [39]. Such a phenomenon, which is considered to be a manifestation of Ostwald's step rule [4], has also been found in some other model systems [40–43]. In the case of hard-core Yukawa system when $1/\kappa d$ is small, the interaction between particles is rather short-ranged to make the colloidal particles act as effective hard spheres. Therefore it is natural to see that the nucleation of hard-core Yukawa system in such a situation also behaves close to that of hard-sphere system. However, there is still a little difference between hard-core Yukawa system under small Debye screening length and hard-sphere system. Here one may observe a few bcc particles during the crystallization process (Figure 2), but it is hard for hard spheres to find bcc crystal structure.

For a direct and clearer investigation of the kinetic process of the crystallization, Figure 3 shows some snapshots of the system's nucleation at $1/\kappa d=0.1$. Previous experiments, theory and computer simulations have already revealed the existence of two-stage scenario in the crystallization process of fluids [10–15]. First, an amorphous precursor with relative dense or relative ordered liquid structure

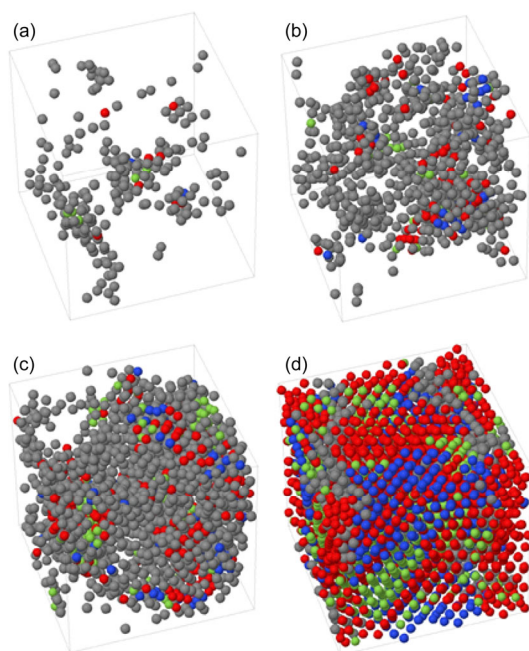


Figure 3 Snapshots of a nucleation and growth event when $1/\kappa d=0.1$. Gray spheres represent liquid particles with $Q_6(i) \geq 0.3$, while liquid particles with $Q_6(i) < 0.3$ are not displayed in the pictures. Red, green and blue spheres represent fcc, hcp and bcc particles, respectively. (a) Configuration at 10^3 MCS; (b) configuration at 10^4 MCS; (c) configuration at 10^5 MCS; (d) configuration at 5×10^5 MCS. (color online)

forms, accounting for an intermediate crystallization step. Then the precursor, during the actual crystallization process, develops into a crystalline phase that is determined by the nature of the interparticle interaction. Afterwards, Tanaka *et al.* [16,17,19] pointed it out that the nucleation process does not consist of discrete steps but is rather continuous. Their work also emphasized the presence of regions where rotational symmetry is broken locally and they act as precursors for nucleation. Such a scenario has been proved to be valid in several systems [10–18]. However, it is still an open question whether this mechanism or the presence of precursors is general in all kinds of nucleation events, especially in the nucleation of charged colloids. Here we define the precursors as the particles with relatively high local order ($Q_6(i) \geq 0.3$) but belong to the level of liquid structures, which are plotted as gray spheres in the snapshots. Crystal (fcc, hcp, and bcc) particles are depicted as colored (red, green and blue) spheres, while the liquid particles with $Q_6(i) < 0.3$ are not displayed in the pictures. From the snapshots displayed in Figure 3, a typical precursor-mediated nucleation and growth event can be seen clearly. At the beginning of nucleation (Figure 3(a)), some clusters that serves as precursors with relatively ordered liquid structures are formed. With the development of the growing precursors, small nuclei emerge from inside region of precursors and then become more and more large, as demonstrated in Figure 3(b, c). It can be seen that the fcc particles are always dominant during the whole process of crystallization. But there are still some bcc and hcp particles in the late nucleation (Figure 3(d)). Afterwards, some fcc particles and most of bcc particles transform into hcp crystal resulting in an equilibrium configuration of mixture with fcc and hcp (see the picture inside the top panel of Figure 1), in accord with the investigation of Figure 2.

Next, we continue to increase the Debye screening length and observe the crystallization of the system. Approximately from $1/\kappa d=0.15$ to $1/\kappa d=0.35$, the crystal structures of the system obtained eventually are always the mixture of fcc, hcp and bcc. Notice that the thermodynamically stable phase of the system is fcc, so both hcp and bcc are indeed metastable phases. As is known, the range of the repulsive interaction among particles is increased with the increasing of Debye screening length. This means that the colloidal particles are no longer like effective hard spheres because they can “feel” more particles of longer distance. To show a typical crystallization event, the curves of the number of fcc, hcp and bcc particles versus MCS during the crystallization when $1/\kappa d=0.25$ are given respectively in Figure 4. In the early stage of crystallization, fcc particles slightly dominate over hcp and bcc particles. Apparently all kinds of the crystal particles increase with the growth of nucleus, but bcc crystal particles seem to increase faster in the late stage of crystallization. Seen from Figure 4, the number of bcc particles at about 1.5×10^6 MCS dominate over fcc and hcp particles. Of course, the crystal structures (e.g, the fraction of

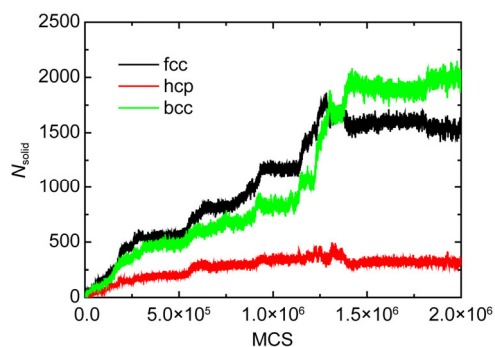


Figure 4 The number of solid (fcc, hcp, and bcc) particles evolves during a SMC simulation when $1/\kappa d=0.25$. (color online)

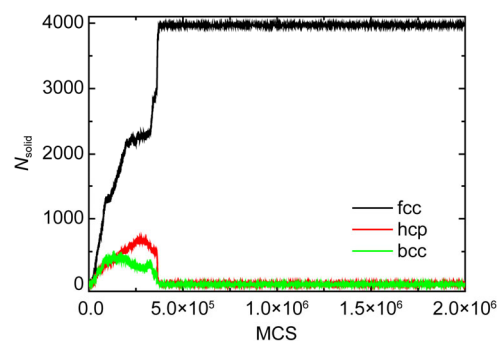


Figure 5 The number of solid (fcc, hcp, and bcc) particles evolves during a SMC simulation when $1/\kappa d=0.4$. (color online)

fcc, hcp and bcc) obtained are somewhat determined by the initial configuration. And bcc particles are not always dominant in the equilibrium system when several simulations at the same value of $1/\kappa d$ are performed independently. Nonetheless, the metastable phases including both bcc and hcp structures do emerge markedly and exist in the system for very long time. Actually we have carried out a few much longer simulations with typically 10^7 MCS, assuring that the metastable structures of both bcc and hcp can not eventually rearrange into thermodynamically stable fcc crystal.

When the Debye screening length is increased to $1/\kappa d=0.4$ or higher values where the crystallization happens, almost all of the colloidal particles in the system can finally become fcc crystal, and there are only very few metastable hcp and bcc particles left. Seen from Figure 5, fcc particles are always dominant in the system during the process of crystallization. Although both hcp and bcc particles do emerge, the number of them is relatively rather small compared with the number of fcc particles. Moreover, the life time of metastable hcp and bcc structures are very short, which is demonstrated in Figure 5: both N_{hcp} and N_{bcc} do reach to a maximum but immediately decreases to almost zero indicating that hcp and bcc structures have transformed into fcc structure. Some snapshots of the configuration during a typical crystallization event are shown in Figure 6. In the early stage of the crystallization, the precursors with $Q_6(i) \geq 0.3$ form and grow in the fluid, and the birth of crystal nuclei afterwards occurs inside the regions of the precursor, which is similar to the case of $1/\kappa d=0.1$ (Figure 3). The core of the nucleus is mostly occupied by fcc particles with only few hcp and bcc particles attached. In the later stage of the crystallization, both hcp and bcc particles can make rearrangement so as to become fcc particles completely, since the interaction range between the colloidal particles is long enough. This final configuration obtained means that the system has eventually achieved a thermodynamically stable phase (fcc).

We would like to mention that the polymorph selection also takes place in point Yukawa system (without the hard-core potential) which has been reported by Desgranges and

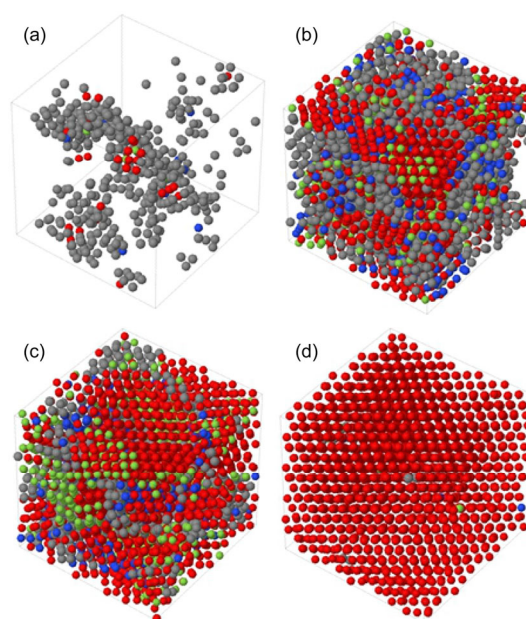


Figure 6 Snapshots of a nucleation and growth event when $1/\kappa d=0.4$. The representation of the spheres shown in the pictures is the same as that of Figure 3. (a) Configuration at 10^4 MCS; (b) configuration at 10^5 MCS; (c) configuration at 3×10^5 MCS; (d) configuration at 4×10^5 MCS. (color online)

Delhommelle [20,21]. Similar to the investigations of our present work, the polymorphism in point Yukawa system strongly depends on the value of a dimensionless screening parameter λ . When $\lambda=3$, bcc is the stable phase and the crystallization mechanism is straightforward so that bcc formation is always favored. When $\lambda=10$, fcc is the stable phase and the crystallization process become more complex to involve metastable states including fcc, hcp and bcc structures [20,21]. The polymorph selection is demonstrated to be after the nucleation step, i.e., the structure of the crystallites becomes predominantly that of the stable fcc structure well within the growth step. The results of point Yukawa system, especially the case of $\lambda=10$, seem to be in agreement with this work. In the present study of hard-core

Yukawa model, we have used a series of Debye screening length and shown its key role on the polymorph selection. The system tends to nucleate into a mixture of fcc, hcp and bcc crystal structures at intermediate values of Debye screening length, which is similar to the crystallization of point Yukawa system at $\lambda=10$ except that fcc is not always dominant (Figure 4). At small Debye screening lengths, the system behaves like a hard-sphere system to get a mixture of fcc and hcp structures (with very few bcc structures), while at high screening lengths the system eventually reaches to a thermodynamically stable phase (fcc) completely.

The observations of metastable and stable crystal structures also remind us of our group's experimental evidence of metastable bcc to stable fcc phase transition in charged colloids by *in situ* monitoring structural changes with the reflection spectrometer during the colloidal crystallization [6], which is also regarded as a manifestation of the Ostwald's step rule. The experimental data demonstrate that the lifetime of the metastable bcc structure decreases significantly with increasing particle volume fraction. It seems as if there was a volume-fraction window for observers to see the metastable to stable phase (bcc-fcc) transition. Comparable to the experimental finding [6], the present results obtained via computer simulations suggest another condition where the metastable phase can be seen and the exceptions to the Ostwald's step rule: under small Debye screening length, the system of charged colloids can nucleate into metastable structures and only later do the metastable structures transform into stable structure (fcc), which is possibly able to be detected by experiments; as the Debye screening length is large enough, the intermediate or metastable phase does probably exist, but always transforms into stable phase very soon so as to make the visualization of such a metastable phase almost impossible in experiments.

4 Conclusions

The hard-core Yukawa model can to some extent represent the effective interactions between charge-stabilized colloidal particles. In this study, we perform SMC simulations to investigate the crystal polymorph and nucleation process of hard-core Yukawa system. The contact value of hard-core Yukawa potential is fixed as $\beta\epsilon=81$, the truncation of interactions $r_{\text{cut}}=1.9$, and the volume fraction of the system is taken as $\phi=0.3$ so that the system can have a large stable phase region of fcc crystal structure. The Debye screening length $1/\kappa d$ can be tuned. We have observed and confirmed that the precursors with relatively ordered liquid structure do emerge in the early stage of nucleation in the hard-core Yukawa fluid. Although the crystal structure of stable phase is fcc lattice, the system crystallizes into a mixture of both fcc and hcp under the small Debye screening length (typi-

cally $1/\kappa d=0.1$) where the colloidal particles act as effective hard spheres. In the intermediate range of Debye screening length (approximately from $1/\kappa d=0.15$ to $1/\kappa d=0.35$), the crystal structures of the system obtained are always the mixture of fcc, hcp and bcc phases. Our findings, i.e. the existence of metastable phases, can be interpreted as a manifestation of the Ostwald's step rule. Until the value of Debye screening length reaches to a large enough value ($1/\kappa d \gg 0.4$), the fcc structure becomes the dominant phase both from a thermodynamic and kinetic point of view. Here we should stress that the present findings may shed light on the molecular mechanisms underlying polymorph selection for charged colloids. Furthermore, our simulations have proved that controlling polymorphism of the crystallization in hard-core Yukawa system is feasible by simply varying the value of Debye screening length.

Finally, we should point it out that the Debye screening length and the contact value are often correlated together in real charge-stabilized suspensions. Hence, it can't easily be done in experiments for the fixed $\beta\epsilon$ and varying $1/\kappa d$ solely. For instance, a variation in κ will change ϵ unless some other parameter, such as the charge of the colloid, is varied at the same time. Nonetheless, our findings via computer simulations shows a possible pathway and condition for the investigation on the metastable and stable phases, as well as the polymorph selection in the crystallization of charge-stabilized colloids.

Acknowledgments This work was supported by the National Natural Science Foundation of China (11172302, 11302226, 10972217), and the Opening Fund of State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, China (LNM201503).

Conflict of interest The authors declare that they have no conflict of interest.

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