Dependence of crystallization of Brownian particles by sedimentation on the force direction

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Masahide Sato*, Muhammad Yusuf Hakim Widianto[1,2], and Youhei Kanatsu[1]

Information Media Center, Kanazawa University, Kanazawa 920-1192, Japan
[1]*Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa 920-1192, Japan*
[2]*Physics of Earth and Complex Systems, Institute of Technology Bandung, Jl Ganesha 10 Bandung 40132, Indonesia*

The formation of a large close-packed colloidal crystal with the fcc structure was observed during the sedimentation of colloidal particles in an inverted pyramidal pit [S. Matsuo et al., Appl. Phys. Lett. **82**, 4285 (2003)]. Carrying out Brownian dynamics simulations, we confirmed that large grains with the fcc structure are formed when the apex angle of the inverted pyramidal container is suitable and the force direction is parallel to the the center axis [Y. Kanatsu and M. Sato, J. Phys. Soc. Jpn. **84**, 044601 (2015)]. To form a high-quality colloidal crystal without defects, it is important to investigate in detail how the quality of a colloidal crystal is affected by the force direction and container shape. In this paper, we focus on the effect of the force direction on crystal quality and investigate how the ratio of the number of the hcp structured particles, $N_{\rm hcp}$, to that of fcc structured particles, $N_{\rm fcc}$, is affected by the force direction. In our simulation, the ratio of $N_{\rm fcc}$ to $N_{\rm hcp}$ is hardly changed when the force direction deviates from the central axis: $N_{\rm fcc}$ is much larger than $N_{\rm hcp}$ irrespective of the force direction. Thus, our results show that the crystal structure is insensitive to the force direction in forming a colloidal crystal by sedimentation in an inverted pyramidal container.

1. Introduction

A colloidal crystal is one of the candidate materials of photonic crystals. For example, a close-packed colloidal crystal with the face-centered cubic (fcc) structure is used as a template for an inverse opal with a three-dimensional full photonic band gap.[1)] Sedimentation[2–20)] is often used in order to form the close-packed colloidal crystals. When colloidal particles precipitate on the flat bottom wall during sedimentation, a triangular lattice is formed on the wall. The lattice acts as the {111} face of the fcc crystal, and a colloidal crystal with the {111} growing interface is formed. In this case, a polycrystal consisting of small grains is formed because many small nuclei arise in the initial stage.

*E-mail: sato@cs.s.kanazawa-u.ac.jp

In addition, two types of stacking method are possible on the {111} face, so that a mixture of the hexagonal close-packed (hcp) and the fcc structures is formed[2,8,12–16] although the fcc structure is more stable than the hcp structure.[21,22] When we try to use colloidal crystals for devices, the formation of a mixture of small grains with different structures should be prevented.

Fabricating the bottom wall of a container[3,4,9,17,18] is one of the ways to prevent the formation of a mixture of different types of small grains. Recently, van Blaaderen *et al.* used the method called colloidal epitaxy to prevent the formation of a mixture of fcc and hcp structured particles.[3] In their method, a pattern with a square lattice is formed on the bottom wall. If the lattice constant is suitable for colloidal particles, the square lattice, which is the {100} face of the fcc structure, is formed on the substrate. The stacking method is unique on the {100} face of the fcc structure, so that large grains with the colloidal crystal with the fcc structure can grow without the formation of the hcp structure. Colloidal epitaxy is a highly potential method, but it is necessary to form the lattice precisely.

Using a pyramidal container is another method to prevent the formation of different types of grain. Recently, Matsuo and coworkers[5,6] succeeded in forming a large colloidal crystal with the fcc structure by a simpler method: they used an inverted pyramidal pit as a container and carried out the sedimentation of colloidal particles. During sedimentation, a triangular lattice, which acts as the {111} face of the fcc structure, is formed on the four side walls of the pyramidal pit. When the apex angle of the pit is suitable, the growing interface becomes the {001} face of the fcc structure and the fcc structure grows without forming defects irrespective of particle size.

Previously, we carried out Brownian dynamics simulation and confirmed that large grains with the fcc structure are formed in the inverted pyramidal container.[20] In the simulation, the force direction was parallel to the central axis. When the force direction deviates from the central axis, the growing interface is tilted from the {100} face of the fcc structure, which may cause the increase in the number of defects in the bulk. If the increase in the number of the defects is sensitive to force direction, we need to control it precisely in order to form high-quality colloidal crystals. Thus, it is necessary to investigate how the quality of colloidal crystals is affected by the force direction and container shape.

In this paper, we focus on the effect of the force direction and carry out Brownian dynamics simulations. We investigate how the bulk structure is affected by the deviation

of the force direction. In Sect. 2, we introduce our model and order parameters. In Sect. 3, we show the results of our simulations. In Sect. 4, we summarize our results.

2. Model and order parameters

In our simulation, we use a simple model, in which particles receive large resistance proportional to their velocity.[12–16,20] The equation of motion of the ith particle is approximately given by

$$\frac{\mathrm{d}\boldsymbol{r}_i}{\mathrm{d}t} = \frac{1}{\zeta}\left(\boldsymbol{F}_{\mathrm{ext}} - \sum_{i\neq j}\boldsymbol{\nabla}U(r_{ij}) + \boldsymbol{F}_i^{\mathrm{B}}\right), \tag{1}$$

where ζ is the frictional coefficient and $\boldsymbol{r}_i$ is the position of the ith particle. The force $\boldsymbol{F}_{\mathbf{ext}}$ is the uniform external force, which causes the sedimentation of particles. The second term represents the interaction between particles. The interaction potential between the ith and jth particles is given by $U(r_{ij})$, where $r_{ij} = |\boldsymbol{r}_i - \boldsymbol{r}_j|$. Since the interaction potential is considered to be a short-range repulsion in an experiment,[5] for simplicity we use the Weeks−Chandler−Anderson (WCA) potential given by[23]

$$U(r_{ij}) = \begin{cases} 4\epsilon\left[\left(\dfrac{\sigma}{r_{ij}}\right)^{12} - \left(\dfrac{\sigma}{r_{ij}}\right)^{6} + \dfrac{1}{4}\right] & (r \leq 2^{1/6}\sigma), \\ 0 & (r \geq 2^{1/6}\sigma). \end{cases} \tag{2}$$

In Eq. (1), the third term $\boldsymbol{F}_i^{\mathrm{B}}$ represents the random force and satisfies $\left\langle \boldsymbol{F}_i^{\mathrm{B}} \right\rangle = \boldsymbol{0}$ and $\left\langle F_{l,i}^{\mathrm{B}}(t) F_{m,i}^{\mathrm{B}}(t') \right\rangle = 2\zeta k_{\mathrm{B}} T \delta_{lm}\delta_{ij}\delta(t-t')$, where $F_{l,i}^{\mathrm{B}}(t)$ is the random force component in the l direction acting on the ith particle. One of the simplest difference equation of eq. (1) is given by[24]

$$\tilde{\boldsymbol{r}}_i(\tilde{t}+\Delta\tilde{t}) = \tilde{\boldsymbol{r}}_i(\tilde{t}) + \left(\tilde{\boldsymbol{F}}_{\mathrm{ext}} - \sum_{i\neq j}\boldsymbol{\nabla}U(\tilde{r}_{ij})\right)\Delta\tilde{t} + \Delta\tilde{\boldsymbol{r}}_i^{\mathrm{B}}, \tag{3}$$

where the particle positions, time, and forces are scaled as $\tilde{\boldsymbol{r}}_i = \boldsymbol{r}_i/\sigma$, $\tilde{t} = t\epsilon/\zeta\sigma^2$, and $\tilde{\boldsymbol{F}}_{\mathrm{ext}} = \boldsymbol{F}_{\mathrm{ext}}\sigma/\epsilon$, respectively. The last term $\Delta\tilde{\boldsymbol{r}}_i^{\mathrm{B}}$ is the normalized displacement by the random force. It satisfies $\left\langle \Delta\tilde{\boldsymbol{r}}_i^{\mathrm{B}} \right\rangle = \boldsymbol{0}$ and $\left\langle \Delta r_{l,i}^{\mathrm{B}}(t)\Delta r_{m,j}^{\mathrm{B}}(t') \right\rangle = 2\tilde{R}^{\mathrm{B}}\Delta\tilde{t}\delta_{ij}\delta_{lm}\delta(t-t')$, where $\Delta r_{l,i}^{\mathrm{B}}(t)$ represents the scaled random displacement component in the l direction and $\tilde{R}^{\mathrm{B}} = k_{\mathrm{B}}T/\epsilon$.

We determine the local structure using three order parameters, d_l, Q_l, and w_l.[8,25–30] The parameter $d_l(i,j)$[8,25] is defined as

$$d_l(i,j) = \sum_{m=-l}^{l} q_{l,m}(i) q_{l,m}^{*}(j), \tag{4}$$

where

$$q_{l,m}(i) = \frac{1}{n_{\rm n}} \sum_{j=1}^{n_{\rm n}} Y_l^m(\theta_{ij}, \phi_{ij}), \tag{5}$$

and $q_{l,m}^*(j)$ is the complex conjugate of $q_{l,m}(j)$. In Eq. (5), $n_{\rm n}$ is the number of neighboring particles, $Y_l^m(\theta_{ij}, \phi_{ij})$ is the spherical harmonics, and θ_{ij} and ϕ_{ij} represent the polar and azimuthal angles, respectively. The repulsion in the WCA potential acts when $r_{ij} < 2^{1/6}\sigma$. Thus, taking the random displacement into account, we treat the ith and jth particles as neighbors if $r_{ij}/(2^{1/6}\sigma) < 1.1$. When $d_6(i,j) > 0.7$, we regard that the connection between the two particles is solidlike. If the number of solidlike connections is larger than 4, the ith particle is considered to be a solid-like particle.

In our simulation, the hcp and fcc structures are formed as close-packed structures. To distinguish them, we use $Q_l(i)$ and $w_l(i)$.[26–30] The parameters $Q_l(i)$ and $w_l(i)$ are defined as[26]

$$Q_l(i) = \sqrt{\frac{4\pi d_l(i,i)}{(2l+1)}}, \tag{6}$$

$$w_l(i) = \sum_{m_1,m_2,m_3} \begin{pmatrix} l & l & l \\ m_1 & m_2 & m_3 \end{pmatrix} \frac{q_{l,m_1}(i) q_{l,m_2}(i) q_{l,m_3}(i)}{d_l(i,i)^3}, \tag{7}$$

where $-l \le m_1, m_2, m_3 \le l$ and $m_1 + m_2 + m_3 = 0$. The term in parentheses in Eq. (7) is the Wigner 3-j symbol. When $n_{\rm n} < 10$, we cannot determine the local structure precisely in some cases because the number of neighbors is small. Thus, we calculate $Q_l(i)$ and $w_l(i)$ and determine the local structure when $n_{\rm n} \ge 10$. The local structure around the ith particle is regarded as the fcc structure if $-0.18 < w_4(i) < -0.01$ and $0.175 < Q_4(i) < 0.2$, and as the hcp structure if $0.02 < w_4(i) < 0.15$ and $0.06 < Q_4(i) < 0.15$. The criteria are the same as those used in our previous studies[14–16,20] and consistent with those used in previous studies by other groups.[26–30]

3. Results of simulations

In our simulations, we use inverted pyramidal containers. The positions of four corners in the bottom wall, A, B, C, and D, are given by $\mathrm{A}(L, 0, L/n_{\rm w})$, $\mathrm{B}(0, L, L/n_{\rm w})$, $\mathrm{C}(-L, 0, L/n_{\rm w})$, and $\mathrm{D}(0, -L, L/n_{\rm w})$, respectively. The position of the apex O is given by $(0, 0, 0)$. The unit normal vectors of the side walls, OAB, OBC, OCD, and ODA, are given by $(n_{\rm w}, n_{\rm w}, 1)/\sqrt{2+n_{\rm w}^2}$, $(-n_{\rm w}, n_{\rm w}, 1)/\sqrt{2+n_{\rm w}^2}$, $(n_{\rm w}, -n_{\rm w}, 1)/\sqrt{2+n_{\rm w}^2}$, and $(-n_{\rm w}, -n_{\rm w}, 1)/\sqrt{2+n_{\rm w}^2}$, respectively. The number of particles $N = 23328$ and the volume fraction $\rho = 0.1$. We carry out simulations by fixing N, ρ, and $n_{\rm w}$. The length L

is given by $L = (2\pi n_{\rm w} N/\rho)^{1/3}\sigma$. Initially, we put particles in the container at random and move them without an external force in order to eliminate the effects of the initial condition. Then, we set the time to be 0 and start simulations by adding the external force.

In our previous study,[20] the force direction was parallel to be $(0, 0, -1)$ and $n_{\rm w} = 1$. Here, in order to focus on the effect of the deviation of the force direction, we set the inclination of the side walls to be $n_{\rm w} = 1$. Shifting the force direction from $(0, 0, -1)$, we investigate how the bulk structure is affected by the deviation of the force direction.

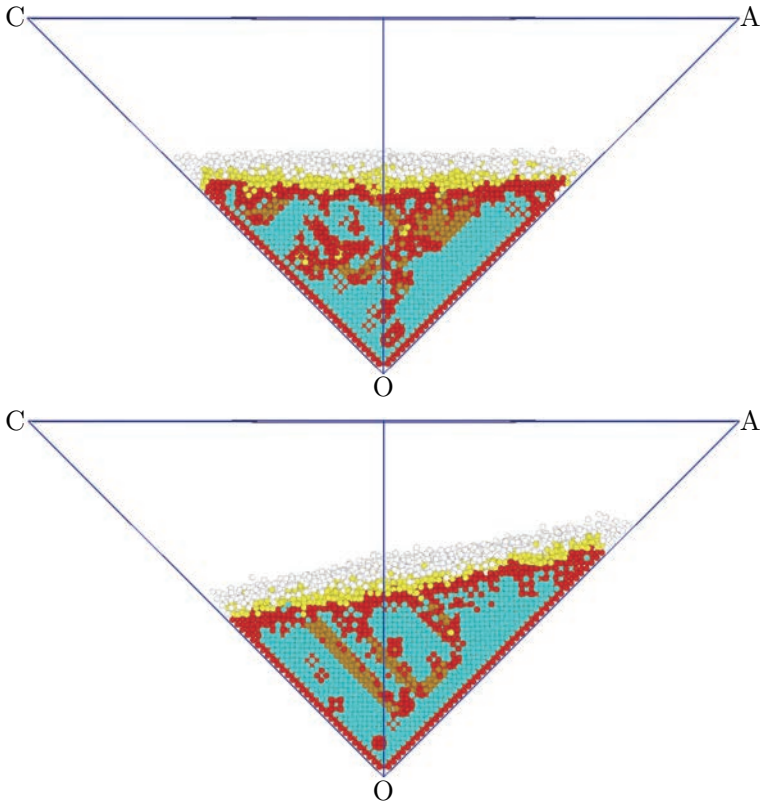

Fig. 1. (color online) Snapshots in a late stage ($\tilde{t} = 400$) with (a) the force in $-z$-direction ($\theta = 0°$ and $\phi = 0°$), and (b) the tilted force ($\theta_{\rm F} = 10°$ and $\phi_{\rm F} = 0°$). The strength of the external force, $F_{\rm ext}$, is given by $F_{\rm ext} = 0.4$.

Figure 1 shows snapshots in the bulk structure, in which the container is cut at the OAC plane. The bulk structure is seen from the negative y-direction. In the snapshots, the particles with the fcc and hcp structures are shown in blue (the third darkest) and orange (the second darkest), respectively. Disordered solidlike particles are in red (the darkest), dilute liquidlike particles are colored white (the brightest) and the dense

liquidlike particles (the second brightest) are in yellow. The force direction is $(0, 0, -1)$ in Fig. 1(a). The hcp structured particles are seen near the solid-liquid interface. In Fig. 1(b), the force direction is given by $(\sin\theta_{\rm F}\cos\phi_{\rm F}, \sin\theta_{\rm F}\sin\phi_{\rm F}, -\cos\theta_{\rm F})$ with $\theta_{\rm F} = 10^\circ$ and $\phi_{\rm F} = 0^\circ$. The lines consisting of the hcp particles, which are parallel to OC, indicate sheetlike grains with the hcp structure.

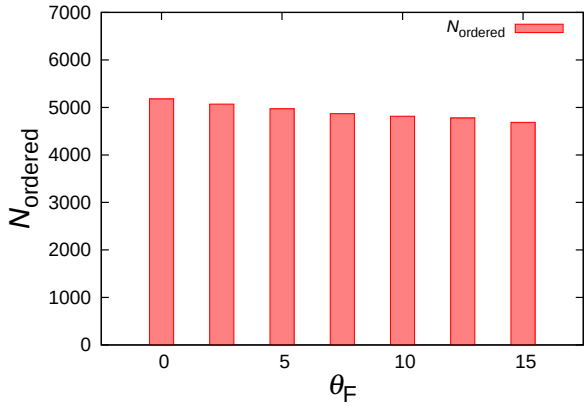

Fig. 2. (color online) Dependence of $N_{\rm ordered}$ on the angle $\theta_{\rm F}$ with $\phi_{\rm F} = 0^\circ$. The strength of the external force $F_{\rm ext}$ is given by $F_{\rm ext} = 0.2$. The data are averaged over 10 samples.

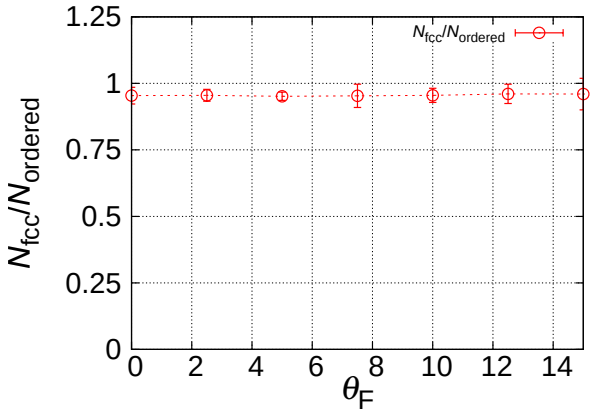

Fig. 3. (color online) Dependence of the ratio of $N_{\rm fcc}$ to $N_{\rm ordered}$ on the angle $\theta_{\rm F}$ with $\phi = 0^\circ$. The strength of the external force $F_{\rm ext}$ is given by $F_{\rm ext} = 0.2$. The data are averaged over 10 samples.

We investigate the dependence of the formation of the hcp structure on the force direction in more detail. Figure 2 shows the dependence of the number of ordered particles, $N_{\rm ordered}$, on the polar angle $\theta_{\rm F}$, where $N_{\rm ordered}$ represents the sum of the number of fcc structured particles, $N_{\rm fcc}$, and that of the hcp structured particles, $N_{\rm hcp}$. With

increasing θ_F, $N_{ordered}$ seems to decrease slightly. However, considering the increase in the volume of the uppermost region formed by the liquidlike particles with the tilted external force, the dependence of $N_{ordered}$ on θ_F seems to be very weak. Figure 3 shows the dependence of the ratio of N_{fcc} to $N_{ordered}$. The ratio is high and hardly depends on θ_F, so that the hcp structure is hardly formed irrespective of θ_F.

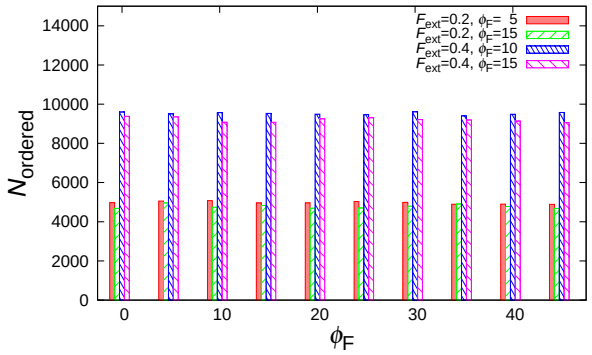

Fig. 4. (color online) Dependence of $N_{ordered}$ on ϕ_F with various θ_F and F_{ext}. The sets of parameters θ_F and F_{ext} are $(\theta_F, F_{ext}) = (5°, 0.2)$, $(15°, 0.2)$, $(10°, 0.4)$, and $(15°, 0.4)$. The data are averaged over 10 samples.

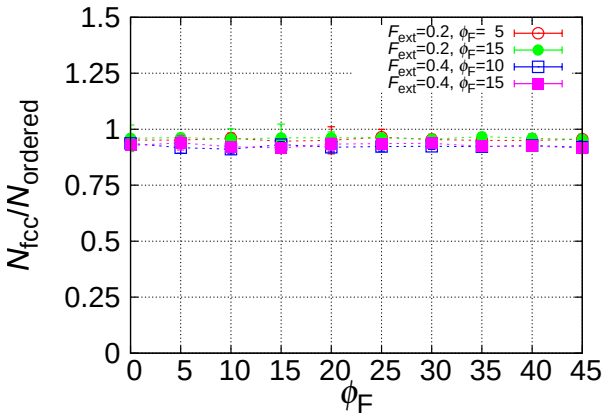

Fig. 5. (color online) Dependence of the ratio $N_{fcc}/N_{ordered}$ on ϕ_F with various θ_F. and F_{ext}. The sets of parameters θ_F and F_{ext} are $(\theta_F, F_{ext}) = (5°, 0.2)$, $(15°, 0.2)$, $(10°, 0.4)$, and $(15°, 0.4)$. The data are averaged over 10 samples.

We also investigate the effect of azimuth ϕ_F on the bulk structure. Figures 4 and 5 show the dependences of $N_{ordered}$ and the ratio $N_{fcc}/N_{ordered}$ on ϕ_F with various θ_F and F_{ext}. Both $N_{ordered}$ and $N_{fcc}/N_{ordered}$ increase with increasing F_{ext}, but do not depend

on the angle ϕ_{F}.

4. Summary

Carrying out the Brownian dynamics simulations with the uniform external force, we studied how the bulk structure is affected by the force direction. From Figs. 2 and 3, the number of the ordered particles N_{ordered} and the ratio of the number of fcc structured particles to that of the ordered particles, $N_{\mathrm{fcc}}/N_{\mathrm{ordered}}$, hardly depend on θ and ϕ. Thus, our simulation suggests that the bulk structure is not sensitive to the force direction.

Now, we do not have a simple idea to explain why the bulk structure is not affected by the force direction. It may be important that the growing interface is the {100} face when the force is in the $-z$-direction. The stacking method is unique on the {100} face of the fcc structure. Naturally, the frequency of remaining disordered particles is low. Thus, the ratio $N_{\mathrm{fcc}}/N_{\mathrm{ordered}}$ is hardly changed when the force direction slightly deviates. The effect of the force direction may become remarkable for different growing interfaces. To clarify the reason why the bulk structure is not sensitive to the force direction, we need to investigate the dependence of the force direction more carefully.

In this paper, we focused on the force direction and did not consider the dependence of the shape of the pyramidal container. The normal direction of the side walls of the pyramidal container, n_{w}, is set to be $n_{\mathrm{w}} = 1$. The fcc structure whose {111} faces are on the side walls can be formed in the container without forming defects in the bulk. Considering the geometrical relationship, however, the disordered particles have to remain in the bulk when $n_{\mathrm{w}} \neq 1$. When the force direction is tilted, not only the number but also the distribution of the disordered particles may be affected by the force direction in an unsuitable container. Now, we intend to study the effect of the force direction on crystallization in an unsuitable container in detail.

Acknowledgments

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