Crystal structure of hard spheres under gravity by Monte Carlo simulation

Atsushi Mori a,*, Shin-ichiro Yanagiya a, Yoshihisa Suzuki b, Tsutomu Sawada c, Kensaku Ito d

a Department of Optical Science and Technology, Faculty of Engineering, The University of Tokushima, 2-1 Minamijosanjima, Tokushima 770-8506, Japan
b Department of Chemical Science and Technology, Faculty of Engineering, The University of Tokushima, 2-1 Minamijosanjima, Tokushima 770-8506, Japan
c National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
d Department of Material Systems Engineering and Life Science, Faculty of Engineering, Toyama University, 3190 Gojuku, Toyama 930-8555, Japan

Abstract

Monte Carlo simulations were performed for hard spheres (HSs) under gravity. The gravity was increased stepwise. HSs were placed between the bottom and the top hard walls. For $g^* > 0.9$, we observed that a ‘sediment’ was comprised of two crystalline and one fluid regions. Here, $g^*$ is defined by $g^* = mg/\kappa T$ with $m$ being the mass of a particle, $\sigma$ the HS diameter, $g$ the acceleration due to gravity, and $\kappa T$ the temperature multiplied by Boltzmann’s constant. The bottom crystal was less defective or well-ordered and the crystal lay between the bottom one and the fluid phase was defective or less-ordered. In this paper, we investigate the structure of the crystals. Despite no apparent defects, the crystal has highly been distorted. That is, the fcc lattice has been contracted in the vertical direction more than in the horizontal direction. The crystal–fluid coexistence condition for the bulk HS system does, in principle, not hold for the present systems at the crystal–fluid interface. In addition, though the fine scale density profile exhibits a discontinuity apparently across the crystal–crystal interface, the interlayer separation increases linearly with the height.

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1. Introduction

Colloidal crystals have drawn interest in recent years as many researchers aim at their use as photonic crystals. Photonic crystals possess spatial periodic modulation of dielectric constant with periodicity of order of the optical wavelength [1–3]. As the typical lattice constant of the colloidal crystals is submicron, some kinds of colloidal crystals can realize the photonic property if the crystallinity is high and the size is large. Various techniques to produce such a large colloidal crystal have recently been developing [4–8].

Nowadays, the hard sphere (HS) model is not a mere idealized model of the colloidal systems [9]. Sterically stabilized colloids, such as poly(methyl methacrylate) (PMMA) microspheres dispersed in a hydrocarbon medium [10–14], exhibit the HS nature with regard to the crystal–fluid phase transition. The phase behavior of the HS system is governed only by the volume fraction of particles, $\phi$.

The system is in a fluid phase for $\phi < 0.494$ and in a crystal (fcc) phase for $\phi < 0.515$ [15], and it means that for $0.494 < \phi < 0.515$, crystal and fluid phases coexist. Though those values were calculated in late 1960s, the coexistence demonstrated by simulations was in the last decade [18–20]. Since the existence of crystalline phase in the HS system was shown by molecular dynamics [16] and Monte Carlo (MC) simulations [17] in 1957, the HS system was studies from a fundamental point of view.

The systems comprised of short-range repulsive interaction crystallize upon the density increase. Indeed, the colloidal dispersions are crystallized by evaporation of the dispersion medium. Sedimentation is another way of the colloidal crystallization relying on this nature. Davis et al. [21] reported fcc structure in a sediment of colloidal silica in 1989. The sedimentation is enhanced by use of a centrifugal rotator. Ackerson et al. [22] reported a centrifugation experiment on a PMMA dispersion. Their result was, however, that when the strength of gravity exceeded 6 G the dispersion froze into a glassy state. Megens et al. [23] reported, on the other hand, that the crystal structure of polystyrene dispersed in ethanol under 400 G was fcc using an X-ray scattering. It is meant that one can cover the wide range of effective gravity region through the use of a centrifugal rotator.
In 1997, Zhu et al. [24] showed that whereas the PMMA suspension formed the random hexagonal closed pack (rhcp) structure under microgravity, the fcc/hcp mixture (or glassy state) appeared under normal gravity. It indicates an effect that the gravity reduces the stacking faults in the HS crystal. Also Kegel and Dhont [25] showed the same tendency, although the structure favored under gravity was not the fcc/hcp mixture but the faulted twinned fcc. The final goal of our simulation study is elucidation of the mechanism of disappearance of the stacking faults due to gravity. The first goal was the development of simulation methods to simulate this phenomenon, avoiding metastable states such as glassy or polycrystalline states, though those states are often observed in the experiment. In other words, we have to sample the related states among the many metastable states. We have accomplished this by the stepwise control of the gravitational number $g^*$, which will be defined in the following paragraph. The major results, which will be published in Ref. [29], are the findings of the defective or less ordered crystalline region above the bottom well-ordered crystal and conversion of that region into the well-ordered crystalline state as $g^*$ increases. In the present paper, as a part of the next step, we make some analyses on the structure we obtained by the simulations.

Biben and co-workers [26,27] already showed the crystallization of HSs at the bottom of a sedimentation profile under gravity by MC simulations. In a previous work [28], we reported that under the same geometry as these the system seemed to be trapped into a polycrystalline metastable state. In the present paper, we report some detail of our MC simulation on the similar system with step-wise controlled gravitational number $g^*$ [29]. Here, $g^*$ is defined by $g^* = mg\sigma/k_B T$ with $m$ being the mass of a particle, $\sigma$ the HS diameter, $g$ the acceleration due to gravity, and $k_B$ Boltzmann’s constant, $T$ the temperature. We note here that, though control of the temperature enables the change of $g^*$, the stepwise control of $g^*$ is efficiently realized by a stepwise control of the aforementioned centrifugation ration rate. In other words, a potential of the use of a centrifugal rotator is implied. In Ref. [29], besides a proposal of a simple method, which is the stepwise $g^*$ control, to avoid the trap, we have found that there exist two crystalline regions; a defective crystalline region exists on a less defective crystalline region at the bottom. The stepwise $g^*$ control, or the stepwise control of centrifugation rotation rate, has a potential of improvement of the crystallinity via the existence of two types of crystals. We investigate here the structure of the crystal, which is influenced by gravity.

2. System and simulation method

We report in this paper on two systems. One includes $N=1664$ HSs in a system with box lengths $L_x = L_y = 6.27\sigma$ and $L_z = 49.23\sigma$. The other $N=3744$ HSs with $L_x = L_y = 9.40\sigma$ and $L_z = 60.\sigma$. The bottom and the top boundaries are fixed, i.e. the hard walls lies, and the periodic boundary condition is imposed in the horizontal direction. The volume fraction of particles is $\phi = 0.45$ and 0.37, respectively, and the number of particles per unit horizontal cross-sectional area is $n_s = 42.3\sigma^2$ for both systems. Some details have been described in Ref. [29].

After preparing the initial fluid state as disordered, we increased the gravitational number $g^*$ stepwise [29]. The gravitational number $g^*$ was increased up to 1.5 and 2.0 with the increment $\Delta g^* = 0.1$ per $2 \times 10^5$ MC cycles (MCCs), respectively, for $N=1664$ and 3744 systems.

3. Results and discussions

3.1. Preliminary

As mentioned already the crystalline region was divided into the bottom less defective (or well-ordered) and the above defective (or less ordered) regions [29]. We should note here on why we have used expressions ‘less defective (or well-ordered)’ and ‘defective (or less ordered)’. Though for the system we report here the upper region includes some defects, in some cases the region is a mere deformed crystal. While for the $N=1664$ system we have observed the fcc crystal with a (001) plane facing the bottom wall, for $N=3744$ system a (111) plane faced the bottom. Some behaviors were quantitatively different from each other; namely, crystal growth direction dependence has been observed. In the (001) growth for $g^* < 0.3$, the bottom crystalline region was not distinguished from the crystalline wetting layer, which occurs along the flat wall in the dense fluid in the HS system [30]. The bottom less defective region grew in an appreciable size when $g^*$ became nearly equal to or slightly greater than 0.8 and its size almost saturated to be about 21$\sigma$ for $g^* > 0.9$. On the other hand, the defective region that appeared at $g^* \approx 0.3$ grew till the appreciable growth of the bottom region began. During rapid growth of the bottom region the defective region shrank, and then with the saturation of the size of the bottom less-defective region the slow growth of the defective crystal started again. In the (111) growth significant layering along the bottom wall took place even at $g^* \approx 0.3$. The less ordered crystalline region above the bottom crystal was not so distinct from the ordering at the crystal–fluid interface till $g^* \approx 0.8$. The height of the well-ordered crystal reached at a saturated value, about 20$\sigma$, already for $g^*$ slightly greater than 0.8. We identified the less ordered region apparently for $g^* > 0.9$. Furthermore, at $g^* \approx 1.4$ an apparent structural change was seen; the intralayer ordering was reduced in appearance although there remained crystalline order (see Fig. 5). We note here that the wetting under the gravitational field is not the subject of the present paper as well as a previous one [29], so we would not deal the details at a low gravitational number such as difference due to the growth direction with regard to the wetting at $g^* \approx 0.3$. Farther, we will not repeat the detail of our previous paper [29], summarizing as in this subsection.

3.2. Snapshots and density profile

In Fig. 1, we plot a snapshot and a density profile at $3.2 \times 10^5$ MCC, at the end of the step of $g^* = 1.5$, for $N=1664$ system. While in Ref. [29] $xz$-projection has been shown,
Fig. 1 (a) is yz-projection; there is no essential difference between the views from xz- and yz-directions, indicating the fourfold rotation symmetry about z-axis. On the other hand, xz- and yz-views are different from each other for the (111) growth. We see, of course, for $N=1664$ system the less defective and defective regions in yz-projection, and in spite of the difference in side views for $N=3744$ system we can identify the defective region in both views. The density profile was calculated by taking spatial average in horizontal direction, as done previously [31]. The reason why Fig. 1(b) is not so smooth is because we have not taken time average. Nevertheless, we can distinguish the less defective and defective regions in the density profile. We can do so for the (111) growth, too. This will be unsuccessful if the horizontal direction does not coincide with one of the crystallographic directions. Fig. 1(c) is a magnification of the defective part of the density profile, from which one can estimate the interlayer spacing. The interlayer separations are, at apparent, almost constant. In the following, we will detect the variation of the interlayer spacing.

3.3. Peak positions and peak separations

We extracted the peak positions, $z_n$, from the numerical data of Fig. 1(b) and plotted in Fig. 2 with the interlayer spacing, $l_n = z_{n+1} - z_n$. These plots for $N=1664$ system at $g^*=1.5$ are fitted by quadratic and linear forms, $z_n/\sigma = 0.0014n^2 + 0.6842n - 0.1176$ and $l_n/\sigma = 0.0032n + 0.685$, respectively. Discrepancy between the derivative of the fitting equation for $z_n$ and the fitting equation for $l_n$ means that the quadratic and linear forms are just approximations. Nevertheless, we can see an increase of the lattice spacing with $n$. In other words, the density decreases as the height increases. This behavior matches the intuition. What is surprising is that the linearity holds despite the discontinuous nature shown in Fig. 1(b).

Effect of defects on the interlayer spacing was not appreciable.
for the present simulations. For $N=1664$ system at $g^*=1.5$, the estimation of $l_n^*=l_n/\sigma$ by the linear approximation are $l_1^*=0.689$ (the most bottom), $l_5^*=0.772$ (the top of the bottom crystal), $l_2^*=0.775$ (the bottom of the upper crystal), and $l_7^*=0.804$ (the top of the upper crystal). Let us compare those with the $a_0=1.57\sigma$, the fcc lattice constant at the crystal–fluid equilibrium, which is calculated from the melting density of the HS crystal, $\rho_m^*=1.04$ ($\phi=0.545$). The interlayer separation along [100] direction corresponding to $a_0$ is $a_0/2=0.785\sigma$. The vertical interlayer separation of the bottom less defective crystal is smaller than $a_0/2$. A result of the full comparison about the defective crystal is that the top five interlayer separations of total 10 separations are larger than $a_0/2$. Similar behaviors were obtained for the other $g^*$’s. There was a tendency that the slope as well as the intercept of $l_n$ decreased with $g^*$ as far as we simulated for $N=1664$ system. Furthermore, the variation of slope exhibits saturation. The increasing property is consequence from the positive compressibility. The saturation is also a natural consequence from the excluded-volume effect. The crystal with its nearest interparticle separation begin the hard core diameter cannot be compressed anymore.

The linearity in $l_n$ was also observed for $N=3744$ system. Let us look at, for example, the linear fits for the interlayer spacing at $g^*=1.5$ and 2.0: $l_n^*=0.0007n+0.822$ and $l_n^*=-0.0002n+0.824$, respectively. The slope decreases and becomes negative at $g^*=1.9$ and 2.0. Decreasing property of the slope is understandable as we have done for $N=1664$ system. A surprising result, the negative slope, needs a detailed discussion. The intercept decreased with $g^*$ and then increased before the slope becomes negative. Those phenomena were not seen for $N=1664$ system. We may encounter such phenomena for larger $g^*$. Or, as a possibility, such phenomena scarcely occur as the nature of the staking behaviors were not seen for $g^*$’s. Or, as a possibility, such phenomena scarcely occur as the nature of the staking.

3.4. Lattice constants and densities

We are more interested in the density (recall that the bulk phase behavior is governed by the density). To this end, we evaluate lattice constants in the horizontal direction. Snapshots of particles projected on to $xy$-plane are shown in Fig. 3 for $N=1664$ system. First of all, we note that [100] and [010] crystal axes are directed in the diagonal directions, so we obtain these square arrays. Recall $L_x/L_y=6.27\sigma$ and be aware that this is equals to $4a_0$; if the crystal structure is the same as that at the crystal–fluid equilibrium, four fcc unit cells lies along $x$- and $y$-axes. In Fig. 3(a) and (b), we see six projections of unit cell (but the unit cell is no longer cubic because it is shrunk in the vertical direction) in the diagonal directions. Therefore, the lattice constant is estimated as $a=1.48\sigma$. We can employ this value for the upper crystal because $6\times6=36$ particles are found in a layer in Fig. 3(c) and (d) despite that the top line is shifted by a half interparticle separation in these figures. We summarize that at the bottom of the system $c=a_0<h_0$ while at the top of the crystal $a_0<c$ where $c$ is the vertical lattice constant. From $a=1.48\sigma$ and the interlayer separations we have estimated above, we find that the density at the top of the defective crystal is about 10% larger than that at the crystal–fluid equilibrium.

Let us evaluate for $N=3744$ system. As already mentioned the crystalline planes, which are stacked in $z$-direction are, the (111) planes as shown in Fig. 4 ($g^*=0.5$) and Fig. 5 ($g^*=1.4$). The interparticle separation in $y$-direction is compared with $a_0\sqrt{2}=1.11\sigma$ and the distance

![Fig. 3. Snapshots (xy-projection) of particles in some layers for N=1664 system at g^*=1.5: (a) the most bottom layer, (b) the top layer of the less defective crystal, (c) the bottom layer of the defective crystal, and (d) the top layer of the defective layer.](image-url)
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between lattice lines in x-direction with $\sqrt{6}a_0/4 = 0.959\sigma$. For both of $g^* = 0.5$ and 1.4, we find 10 lattice lines in x-direction. We have made an image of the regular lattice if the lattice is distorted or disordered, because the lattice constant measured optically or by diffraction is that of ordered parts. Taking into account the effect that the strain of crystalline lattices can be released at the disordered parts such as gain boundaries, this estimation is not so accurate. We find eight and nine particles on a lattice line along y-direction, respectively for $g^* = 0.5$ and 1.5. Accordingly, we evaluate the lattice line separation along x-direction to be 0.940$\sigma$, and the interparticle separation in y-direction 1.17$\sigma$ and 1.04$\sigma$, respectively, for $g^* = 0.5$ and 1.5. The lattice plane was contracted in x-direction by 2.0% as compared to that at the crystal–fluid phase transition. On the other hand, the lattice plane was expanded by 6.1% for $g^* = 0.5$ and contracted by 5.7% for $g^* = 1.5$ in y-direction. The crystals were stressed due to the smallness of the system. In spite of such stress, due to the low interfacial free energy between fcc (111) face and the flat wall, the (111) growth did occur. Let us estimate the density using the linear fits, $l_{n,s}$. In the lower portion of the crystal, the density was higher than that at the crystal–fluid transition for $g^* = 0.5$ and 1.5; the densities were, respectively, 3 and 19% higher at the bottom. For $g^* = 1.5$, the density is higher than that at the crystal–fluid transition even at the top of the upper crystal, which was 14% higher. On the other hand, for $g^* = 0.5$ the density at the top of the upper crystal was 1.4% lower. Traversing from the bottom toward top, the density became lower than that at the crystal–fluid transition at 14th layer, which was just below the crystal–crystal interface. Evolution of crystalline structure in a region where the density is lower than that at the crystal–fluid transition must be an indication of the wetting on the patterned surface by crystalline layers, which has been demonstrated by MC simulations by Heni and Löwen [32,33]. They have shown that the crystalline wetting region becomes thicker on the (111) pattern.

3.5. Discussions

For both of the (001) and (111) growths, the density of the crystal at the crystal–fluid interface did not coincide with that at the bulk crystal–fluid transition [15]. This is in contrast to Kanai et al. [34,35]. They have shown that for the aqueous dispersion of polystyrene microparticles, which is a charge-stabilized colloid, the lattice constant of the crystal at the crystal–fluid interface coincides with that at the crystal–fluid equilibrium even though the system was not only non-uniform but also in non-equilibrium. In the above, we have pointed the effect of wetting on the patterned surface, which makes the density of the crystal lower than that at the crystal–fluid phase transition. Now, let us understand the reason for a case that the coexistence condition in the present simulation has shifted to the high-density region as follows. The crystalline lattice for the (001) growth has been deformed highly due to the periodic boundary condition in the horizontal direction. Distortion increases the free energy of the crystal. Thus, the chemical potential of the crystal we obtained by the present simulation must be higher than the chemical potential at the crystal–fluid equilibrium. Accordingly, the chemical potentials of the crystal and the fluid become equal to each other at the higher density. The height where the vertical interlayer separation becomes larger than
ae/2 for the (001) growth lowers as g* decreases and eventually it locates in the bottom crystalline region. We note here the difference between the origins of the non-uniformity in the present simulation and Kanai et al.’s experiments [34,35]. In the present simulation, the system is in the sedimentation equilibrium in a sense. On the hand, as noted above, the system is in non-equilibrium in Kanai et al.’s experiments. In addition, in their experiment the gravity effect is absent during the melting process of the crystal–fluid coexistence state in the sediment, though the origin itself is the reminiscent of the sedimentation profile under a non-zero gravity. There is a possibility that relaxation of that local density or lattice spacing after the removing gravity is separated from the order–disorder phase transition. Simulation of relaxation process after removing gravity is our forthcoming study.

4. Concluding remarks

We have performed Monte Carlo simulations of hard spheres under gravity. Besides a finding of coexistence of defective and less defective crystalline regions [29], here we have reported on the structure of the crystal. Whereas in the crystal–fluid equilibrium the crystal lattice is fcc, the crystal under gravity in the present simulation was a deformed fcc. At the bottom the vertical lattice spacing was smaller than that of the horizontal one, and the horizontal lattice spacing, which was also smaller than the lattice spacing at the crystal–fluid equilibrium, was determined under the influence from the periodic boundary condition. Near the top of the crystalline region the vertical lattice spacing was larger than the lattice spacing at the crystal–fluid equilibrium. For the (001) growth, nevertheless, the density there was higher than that at the crystal–fluid equilibrium. For the (111) growth, the density of the crystal in the upper region can lower than that at the crystal–fluid equilibrium if the gravitational number is small.

We have, in particular, focused on the density. Among the structural properties, the defect is also of interest and of practical importance. That is, the photonic property must be affected and in case suffered from the defect. Zhu et al. [24] in 1997 reported that in the HS system fcc/hcp mixed states were observed under the normal gravity whereas the crystalline state is of random hexagonal close pack under a microgravity through the experiment using PMMA particles dispersion. Analysis about the defect and mechanism of defect control are now under way.

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