DEFCT BEHAVIOR IN COLLOIDAL CRYSTALS UNDER GRAVITY

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Introduction

In 1997 Zhu *et al.* [1] showed an effect of gravity that reduced defects in colloidal crystals. By comparing the results of colloidal crystallization on the Space Shuttle with those under gravity using hard sphere suspension, they concluded that a sediment was a random hexagonal close pack (rhcp) structure under microgravity while it was mixture of rhcp and face-centered cubic (fcc) crystals under normal gravity. The trend that the gravity reduced the stacking disorder was obtained also by Kegek and Dhont [2]. Their result was, however, that the structure under normal gravity was fauled-twinned fcc instead of rhcp/fcc mixture. The difference, of course, resulted from the difference of the condition of the sedimentation; the particle sizes were different and also the differences between specific gravities of a dispersing particle and dispersion medium were different. In addition, the observed states might be in metasable equilibria; processes between certain metabtable state and another metastable state might be involved in the observation.

The present author and coworkers [3] observed the defect disappearance in the hard-sphere (HS) crystal under gravity in a case of fcc (001) stacking by Monte Carlo (MC) simulations. By close looks they found a glide mechanism of a Shockley partial dislocation for shrinking of an intrinsic stacking fault [4].

Fcc (001) stacking due to the periodic boundary condition

Snapshots of MC simulations of HSs under gravity at $g^*(\equiv mg\sigma/k_B T)$ = 0.9 are shown in Fig. 1, where HSs stacked in fcc (001) due to the stress from a small simulation box. N=1664 HSs were confined in a simulation box of $L_x = L_y = 6.27\sigma$ with the periodic boundary condition (PBC) in xy direction and flat hard walls at $z = 0$ and $z = L_z = 49.23\sigma$. In this simulation g^* was increased by $\Delta g^* = 0.1$ at every 2×10^5 MC cycle (MCC) [3]. Here, the MCC defined such that one MCC contains N particle move. At first, there exit 6 particles along the side axes, despite the L_y being $4a_0$ with a_0 being the fcc lattice constant at the HS crystal-fluid coexistence. This is because there is a pressure gradient according the mechanical balance equation $\partial P/\partial z = -mg\rho(z)$ and thus the pressure at the bottom is lager than that at crystal-fluid coexistence. Here, P is the prssure, m the mass of a particle, g the acceleration due to gravity, $\rho(z)$ the particle number density at the altitude z in coarse scale.

We see that a defect existing in the central region ($z/\sigma \approx$ 8–14) of Fig. 1(a) disappeared in Fig. 1(b). By a close look [4] we revealed that the shrinking of an intrinsic staking fault was mediated by a glide of the Shockley partial dislocation. The Shockley partial dislocation is understood by decomposing a perfect dislocation $\boldsymbol{b}$ = (1/2)[110] (=$\boldsymbol{a}_1/2+\boldsymbol{a}_2/2$ with $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, and $\boldsymbol{a}_3$ denoting the lattice vectors) into $\boldsymbol{b}^{\mathrm{I}} + \boldsymbol{b}^{\mathrm{II}}$ with $\boldsymbol{b}^{\mathrm{I}}$ = (1/6)[211] and $\boldsymbol{b}^{\mathrm{II}}$ = (1/6)[12$\bar{1}$] as described in [5]. The Burgers vectores $\boldsymbol{b}^{\mathrm{I}}$ connects the site A at the corner of the triangle of ($\bar{1}$11) in the unit cell to B just above-deep and coincides with the gap between planes which does and does not undergo the translation by the partial dislocation $\boldsymbol{b}^{\mathrm{I}}$. We observed this gap at the lower end point of the intrinsic stacking fault, which was moving along the glide plane ($\bar{1}$11) [4].

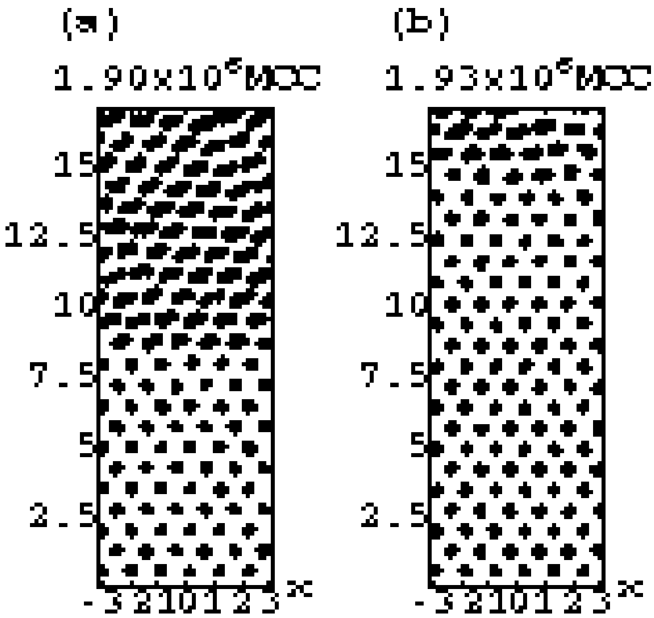

Fig. 1: Snapshots projected onto xz plane at (a) 1.90 and (b) 1.93 $\times10^6$ th MCC (g^* = 0.9).

In this simulation the fcc (001) stacking was induced by the stress from the small PBC simulation box. This was artifact. However, it is noticed that the fcc (001) stacking can be realized by the colloidal epitaxy [6] and we stress that the mechanism we found can occur in the colloidal crystallization. In other words, the stress from the simulation box has the same symmetry as that from the template used in the colloidal epitexy.

If the system size is large, interfacial effect against the bottom wall dominates. For N=3744 system fcc (111) stacking occurred [3]. The interfacial energy against the flat wall is lower when fcc (111) faces the wall [7]. The size effect for fcc (001) growth cannot be investigated by merely doubling the system size.

Fcc (001) stacking due to square pattern

To rule out the artifact that the fcc (001) stacking was caused by the stress from the small PBC simulation box in [3] and [4], we have performed MC simulations of crystallization of HS on a square pattern. The MC simulation of the crystallization of HSs on a square pattern is also the demonstration of corresponding experiment [8]. The advantage of this method is that not only the point-on-point matching but also the point –on-line matching are possible: the particles just above the bottom wall can locate on the line between the lattice point. N=6656 HSs were confined in a simulation box of $L_x = L_y = 12.55\sigma$ with PBC and a patterned wall at z = 0 and a flat wall at $z = L_z = 200\sigma$. Grooves of width 0.707106781σ were in transverse and longitudinal directions with separation 0.338σ on the bottom wall. The diagonal length of the squares of the intersection of the grooves results in 0.9999999997σ; the particle does not fall on to the bottom of the groove. In this simulation g^* was increased by $\Delta g^* = 0.1$ at every 2×10^5 MCC, too.

Snapshots at $g^* = 0.7$ are shown in Fig. 2. At first, the matching between the crystal and pattern is of point-to-point. Comparing Fig.2 (a) and (b) we observe the disappearance of a defect. In Fig. 2(a) the region below $z/\sigma \approx 9$ looks similarly as that in Fig. 1(a) above $z/\sigma \approx 8$. It indicates that there are two or more crystalline planes, which slide relatively such as in the stacking fault terminated by a partial dislocation. A close look at Fig. 2(b) we find a stacking fault; looking for example, at the level $z/\sigma \approx 2.5$ we observe a step at $y/\sigma \approx -1.5$. Disappearance of the defect occured at lower g^* than for the colloidal epitaxy than for flat bottom case, but the disappearance was not complete. It may be due to the large system size. There remains a possibility that the lower value of g^* result, and further increase of g^* and annealing may cause the perfect disappearance. The subsequent analysis of the result will answer.

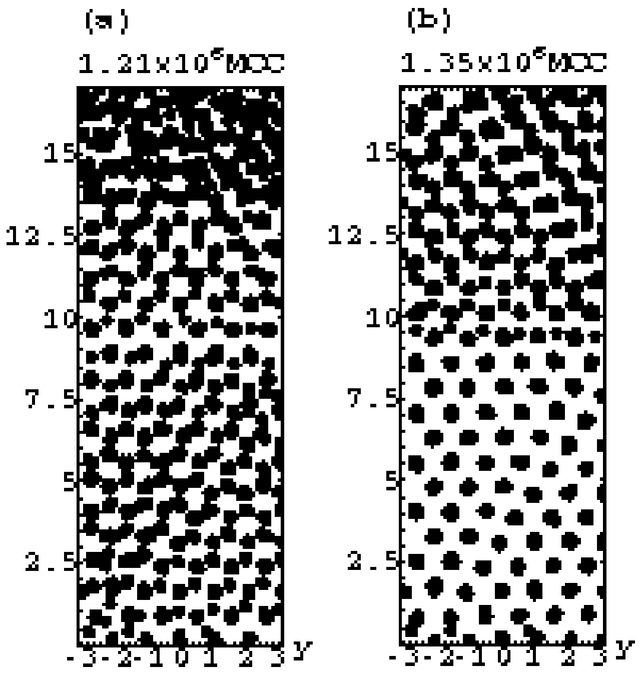

Fig. 2: Snapshots projected onto yz plane at (a) 1.21 and (b) 1.35×10^6 MCC (g^*=0.7).

Concluding remarks

In fcc (001) stacking we observed disappearance of a defect in hard-sphere crystals under gravity. An intrinsic stacking fault shrunk through the glide of the Shockley partial dislocation, which terminates the lower end of the stacking fault. It is an answer to the one-decade long-standing problem; why the defects in colloidal crystals reduce due to gravity. It is also an indication of advantage of the colloidal epitaxy [6], where stacking is fixed by the pattern on the substrate. It is also shown that the substrate pattern decreases g^* where the defect disappearance occurs.

References

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