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Identification of triangular-shaped defects often appeared in hard-sphere crystals grown on a square pattern under gravity by Monte Carlo simulations

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ABSTRACT

In this paper, we have successfully identified the triangular-shaped defect structures with stacking fault tetrahedra. These structure often appeared in hard-sphere (HS) crystals grown on a square pattern under gravity. We have, so far, performed Monte Carlo simulations of the HS crystals under gravity. Single stacking faults as observed previously in the HS crystals grown on a flat wall were not seen in the case of square template. Instead, defect structures with triangular appearance in *xz*- and *yz*- projections were appreciable. We have identified them by looking layer by layer. Those structures are surrounded by stacking faults along face-centered cubic (fcc) {111}. Also, we see isolated vacancies and vacancy–interstitial pairs, and we have found octahedral structures surrounded by stacking faults along fcc {111}.

1. Introduction

In 1997, Zhu et al. discovered an effect of gravity that reduces the stacking disorder in hard-sphere (HS) colloidal crystals [1]. The mechanism of reduction of the stacking defects due to gravity has not been understood for a long time; even if the stacking disorders occur, the particle number density is not affected. We demonstrated the reduction of stacking disorders in the HS crystals under gravity by Monte Carlo (MC) simulations [2]. By close looks at the snapshots of these simulations, we found a glide mechanism of a Shockley partial dislocation for shrink of an intrinsic stacking fault for the HS crystals grown in face-centered cubic (fcc) ⟨001⟩ [3]. A key is fcc ⟨001⟩ stacking; in this stacking the stacking fault runs along oblique {111} and the intrinsic stacking fault is terminated at its lower end by the Shockley partial dislocation. One can understand buoyancy of the Shockley partial dislocation because its dislocation core accompanies a particle deficiency of 1/3 lattice line. Also, the elastic field due to the Shockley partial dislocation yields a driving force for the Shockley partial dislocation to move toward shrinking of the intrinsic stacking fault [4]. That is, the gravity as well as the elastic field gives a driving force for shrinking of the stacking faults. Additionally, we calculated the cross term of elastic fields due to gravity and the Shockley partial dislocation [5]. This term also gives a driving force for shrinking of the staking faults.

In 1993, Biben et al. studied the colloidal crystals under gravity relying on a density functional theory with MC simulations of the HS and screened Coulomb systems [6]. The crystal defect was not their subject; their interest was in computation of density profiles on the basis of macroscopic equilibrium condition and their relation to the interparticle interaction. The number of particles on a unit area of the bottom wall (hereafter n_s^*) was enough large. Thus, the onset of the crystal defect could be seen in a vertical density profile; oscillatory amplitude decreased non-monotonically with the altitude for $n_s^*=40$ and $g^*=0.4$ (the dimensionless quantity g^* is defined as $g^*=mg\sigma/k_BT$, which is an indicator of the strength of the gravity relative to the thermal energy, where m is the (buoyant) mass, g is the acceleration due to gravity, σ is the HS diameter, k_B is Boltzmann's constant, and T is the temperature).

In 1989, Pusey et al. found formation of mixture of fcc and random hexagonal close pack (rhcp), which is random stacking of fcc {111} hexagonal planes, in sediments of an HS colloid under normal gravity by using a laser light scattering [7]. Viewing fcc crystals along ⟨111⟩, the stacking is of ABC type, where A, B, and C stand for the three types of the hexagonal planes on the basis of the lateral position of particles. On the other hand, for hexagonal close-pack (hcp) the stacking sequence is of ABAB type. The rhcp corresponds to the random sequences of A, B, and C. Zhu et al. found that the rhcp forms for the HS colloid in microgravity [1]

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while under normal gravity mixture of rhcp and fcc forms as reported in Ref. [7].

A criticism can arise that the situation in Ref. [3] is unrealizable. That is, fcc ⟨001⟩ stacking there was forced by a small simulation box with the periodic boundary condition (PBC). Against this criticism, we have emphasized that a stress possessing the same symmetry can be realized by using a patterned substrate (template) with the same symmetry. Usage of the template in the colloidal crystallization was proposed by van Blaaderen et al. [8] (the colloidal epitaxy). Recently, we have successfully replaced the driving force for fcc ⟨001⟩ stacking (the stress from a small PBC simulation box) with a stress from a square pattern on the bottom wall [9–11]. We note that the colloidal epitaxy on a square pattern was already demonstrated by Lin et al. [12]. An advantage of the use of square pattern as compared to fcc (001) pattern is that the lattice constant of the crystal grown on the template can, in principle, be adjusted by matching the crystal on the lattice lines instead of the lattice points.

In this way, we have successfully demonstrated the reduction of stacking disorders in the colloidal epitaxy under gravity, and given a reasonable understanding of the mechanism. The reduction of defects has, however, not been perfect. Defect structures with triangular appearance in *xz*- and *yz*- projections have sometimes been appreciable. The main purpose of this paper is to identify those triangular defect structures in a framework of geometrical crystallographic consideration. The defect structures with triangular appearance were already seen in simulations of a small system size [9]. We could, however, not rule out the system size effect. That is, the triangular shapes might be resulted so that stress from the small simulation box be minimized. Indeed, triangular shapes were not isolated with each other. By doubling the horizontal system size, isolated triangular shapes have formed [11]. In this paper, we will take close looks at these defect structures.

It is helpful for understanding the significance of the present study to distinguish the present defect structures from the similar ones. The triangular-shaped defect structures were observed by Meijer et al. [13], de Villeneuve et al. [14], and Hilhorst et al. [15]. Meijer et al.'s observations were, however, in a hexagonal layer (though de Villeneuve et al.'s aim was observations of grains, these were done in the hexagonal layers). That is, triangular-shaped islands formed in an fcc {111} layer in fcc {111} stacking — note that in the present study we investigate fcc (001) stacking. They made three-dimensional (3D) analysis and the islands observed were three-dimensionally extended; however, 3D outer shapes were not put in relieves. The triangular shapes there were purely originated in the difference in lateral stacking position as compared to the surroundings. Meijer et al. made a picture of a 3D dislocation network; however, it was unfortunate that no 3D structures formed by stacking disorders were drawn. Also, Hilhorst et al. showed 2D confocal images, in which the triangular-shaped structures in a horizontal hexagonal layer were seen. The origin of the observed triangular shapes there were in the difference in the lateral positions of the particles in the hexagonal layers, too. Besides, 3D consideration was done. That is, slanted stacking faults were observed; however, no 3D structure formed by stacking disorders was drawn, too. The same situation has been seen in a recent simulation study [16].

The paper is organized as follows. Section 2 describes the system and simulation method. We take layer-by-layer looks for the bottom, middle, and upper regions in Section 3. Although the main purpose is to identify the triangular-shaped defect structures, we analyze other defect structures. In particular, in Section 3.2 the majority of defects is point defects. On the other hand, in Section 3.4 we postpone the conclusion because the defect structure in the upper region seems to be affected by the system size. Identification of the compact triangular-shaped defects structures is done in Section 3.3. We note that, as a first step, we make geometrical crystallographic considerations. Discussion is given in Section 4. Section 5 concludes this paper, along with remarks on future studies.

2. System and simulation

N=26,634 HSs were confined between a flat top wall at $z=L_z$ and a square template at $z=0$. The PBC was imposed in the horizontal x and y directions. The system size was as $L_x=L_y=25.09\sigma$ (thus $n_s^*=42.3$) and $L_z=1000\sigma$. The square pattern on the bottom wall was as follows: the groove width was 0.707106781σ and the side-to-side separation between adjacent grooves was 0.338σ (see Ref. [17] for a note on the significant digits); the numbers of groves along x- and y-axes were 24. The diagonal length of the intersection of the grooves running in x and y directions is, thus, 0.9999999997σ. As a results, an HS did not fall into but fitted to the intersection. An illustration of the square pattern is seen in a chapter of a book [18]. We maintained the gravitational number g^* constant. On the other hand, in early days [9,10], we controlled gravity stepwise as proposed in Ref. [2] as a method to avoid the metastable polycrystalline state. We continued MC simulations for 5.12×10^7 Monte Carlo cycles (MCC). Here, one MCC is defined such that one MCC contains N MC moves. The maximum displacement of the MC move of a particle was fixed at 0.06σ.

A note on g^*, which plays a central role in sedimentation, is given here. This quantity is identical to the reduced inverse

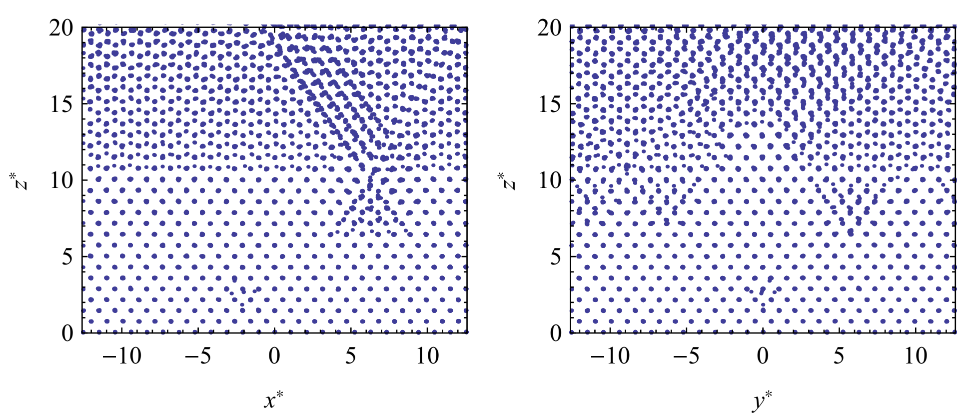

Fig. 1. Snapshot at 4.5×10^7th MCC for $g^*=1.6$: *xz*- (left) and *yz*- (right) projections are shown.