

MONTE CARLO SIMULATION OF DEFECTS IN HARD-SPHERE CRYSTAL GROWN ON A SQUARE PATTERN

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Introduction

An effect of gravity that reduced defects in colloidal crystals was shown in 1997 by Zhu *et al.* [1]. The present author and coworkers [2] observed the defect disappearance in hard-sphere (HS) crystals under gravity in a case of the face-centered cubic (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 [3]. In our simulation the fcc (001) stacking was driven by a stress from the simulation box of a periodic boundary condition (PBC); this was an artifact to be resolved. Experimentally a stress with the same symmetry can be provided by the pattern on a substrate. While van Blaaderen *et al.* [4] proposed the use of a fcc (001) pattern, Lin *et al.* [5] employed a squared pattern. The use of the square pattern has an advantage that the lattice constant can be adjusted by matching on the lattice lines instead of on the lattice points.

We have already resolved this artifact; some results of simulations of a colloidal epitaxy on a square pattern have been reported [6][7]. In these simulations we have employed a step-wise control of g^* ($\equiv mg\sigma/k_B T$ with m being the mass of a particle, g the acceleration due to gravity, σ the HS diameter, $k_B T$ the temperature multiplied by Boltzmann's constant), which was proposed in Ref. [2]. In Ref. [7] we reported a band structure of stacking disorders as sessile. By doubling the lateral system size, however, we observed sessile defects, which were suggested to be stacking tetrahedra [6].

We will report some results of MC simulations with g^* kept constant from the beginning. For flat bottom wall cases if a gravity such as $g^* > 0.9$ was suddenly applied, the system did polycrystallize [8]. This was due to the competition between heterogeneous nucleation near a wall and homogeneous nucleation inside [9]. In

simulations of the colloidal epitaxy the crystal nucleation on the patterned substrate and successive upward growth overcomes [6]. It is suggested that in the case of the colloidal epitaxy we can avoid the polycrystallization without the step-wise control of g^* . We show the time evolution of the center of the gravity for the simulation of Ref. [6] in Fig 1 (a). In this simulation g^* was increased by $\Delta g^* = 0.1$ at every $\Delta t = 8 \times 10^5$ MC cycle (MCC). Here, one MCC is defined such that it contains N MC moves with N being the number of particles. We see that the relaxation during respective g^* stage was incomplete. We are interested in the behavior of the system with enough relaxation.

Simulation

$N = 26624$ HSs were confined in a simulation box of $L_x = L_y = 25.09\sigma$ with PBC and a patterned wall at $z = 0$ and a flat wall at $z = L_z (=1000\sigma)$. Grooves of width 0.707106781σ were formed along transverse and longitudinal directions with separation between the neighboring groove centers being 1.045106781σ on the bottom wall. The diagonal length of the squares of the intersection of the grooves results in 0.999999997σ . Hence, the particle does not fall on to the bottom of the groove. In this paper, we present some results of simulations with constant g^* . A simulation at constant g^* was continued for 5.12×10^7 MCC. The maximum displacement of particles is the same as previous simulations we performed [2][3][6][7].

Results and discussions

Evolutions of the center of gravity for the simulations at constant g^* are shown in Fig.1 (b). While the relaxation at $g^*=0.1$ is obviously incomplete, those at $g^*=0.6, 0.9$, and 1.6 are seemingly enough. By close looks at magnifications, however, the seemingly

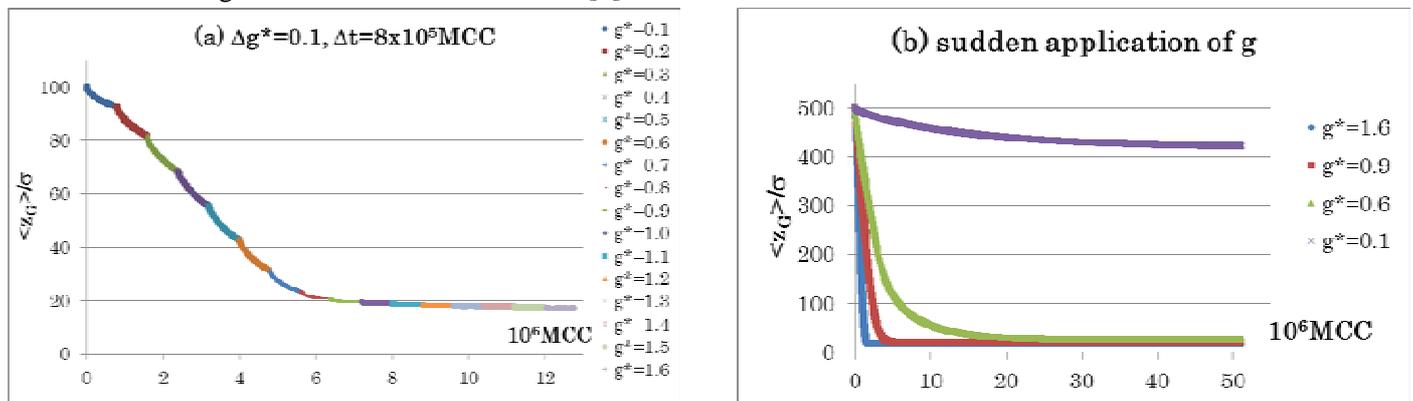


Fig.1: Evolution of the center of gravity for (a) a simulation of with a step-size g^* control [6] and (b) and simulations with suddenly applied g^* .

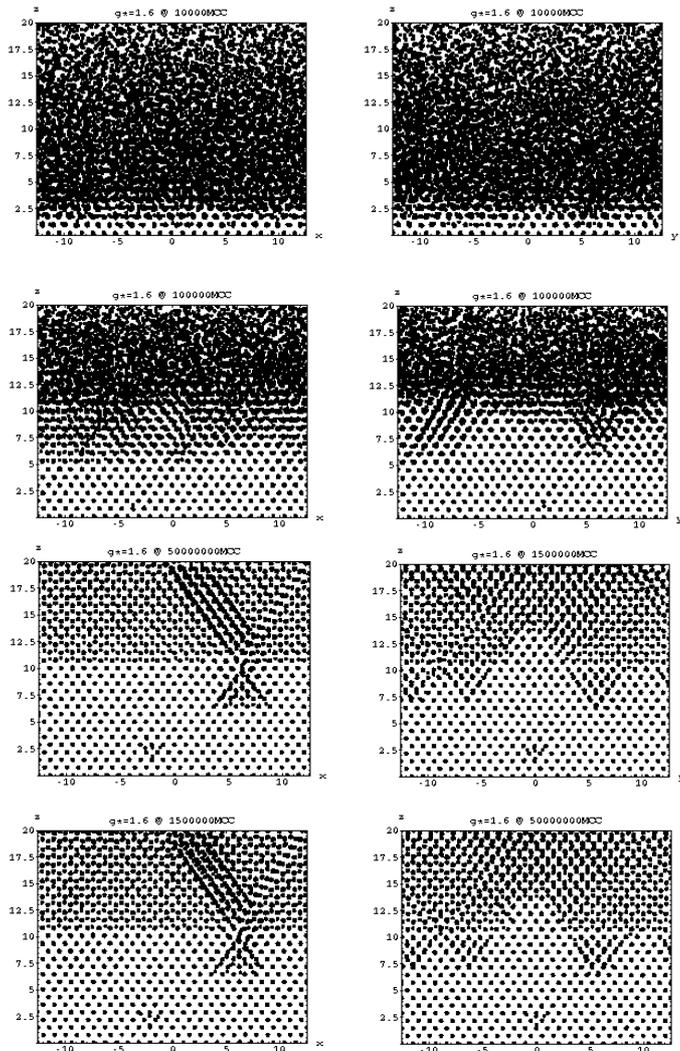


Fig. 2: Projected snapshots of a simulation at $g^*=1.6$.

horizontal parts for $g^*=0.6, 0.9$, and 1.6 are very slightly decreasing lines.

In Fig. 2 we show snapshots at $g^*=1.6$. At 1×10^4 th MCC a few crystalline layers formed epitaxially to the bottom wall with matching on the points are seen. At 1×10^5 th MCC the defect-less crystal at the bottom grew and we see a defective crystal between the defect-less crystal and a disordered phase. The upward motion of the crystal-fluid interface and lowering of the top surface of the fluid occurred during the steep sinking of the center of the gravity at the early stage seen in Fig. 1 (b). At late stage the slight sinking of the center of the gravity is attributed to the defect disappearance; comparing between the snapshots at 1.5×10^6 th MCC and 5×10^7 th MCC we find the transformation of a part of a layer of the defective crystalline phase to the defect-less crystal ($x < 3\sigma, z \sim 11\sigma$). We note also on the existence of defects of a triangular shape. Formation of stacking fault tetrahedra is suggested [6]; the conclusion of Ref. [7] that the band structures of stacking disorders arose should be reconsidered – though from the crystallographic geometrical consideration the band structures such as a twin band are sessile, their occurrence is significantly influenced by the smallness

of the system as compared to the stacking fault tetrahedra. Comparing the snapshots at 1×10^5 th MCC and 1.5×10^6 th MCC we understand that in the crossover region between the steep sinking of the center of the gravity and its slight lowering defect disappearance plays the main role. From the fact that the splitting of the projections of lattice lines vanished, disappearance of stacking disorder is conjectured as in Refs. [3][6][7].

Concluding remarks

Unlike the flat wall case [8], even if we suddenly apply the gravity such as $g^*=1.6$ the system does not polycrystallize in the case of the squared patterned wall. This may be because the crystalline nucleation on the patterned substrate overcomes. Band structures of the stacking disorder, which were reported previously [7], have been avoided by enlarging the lateral system size. Instead, stacking fault tetrahedra have been suggested [6]. Disappearance of stacking disorder is conjectured.

References

- [1] Zhu, J., Liu, M., Rogers, W. Mayer, H. Ottewill, R. H., STS-73 Space Shuttle Crew, Russel, W. B., Chaikin, P. M., Crystallization of hard-sphere colloids in microgravity, *Nature* **387** (1997) 883-885.
- [2] Mori, A., Yanagiya, S.-i., Suzuki, Y., Sawada, T., Ito, K., Monte Carlo simulation of crystal-fluid coexistence state in the hard-sphere system under gravity with stepwise control, *J. Chem. Phys.* **124** (2006) 174507-1-174507-10.
- [3] Mori, A., Suzuki, Y., Yanagiya, S.-i., Sawada, T., Ito, K., Shrinking stacking fault through glide of the Shockley partial dislocation in hard-sphere crystal under gravity, *Molec. Phys.* **105** (2007) 1377-1383; Errata 106 (2008) 187.
- [4] van Blaaderen, A., Ruel, R., Wiltius, P., Template-directed colloidal crystallization. *Nature* **385** (1997) 321-324.
- [5] Lin, K.-h., Croker, J. C., Prasad, V., Schofield, A., Weitz, D. A., Lubensky, T. C., Yodh, G., Entropically Driven Colloidal Crystallization of Patterned Surfaces, *Phys Rev. Lett.* **85** (2000) 1770-1773.
- [6] Mori, A., Monte Carlo simulation of growth of hard-sphere crystals on a square pattern. *J. Cryst. Growth* **318** (2011). 66-71.
- [7] Mori, A., Disappearance of stacking fault in colloidal crystals under gravity, *World J. Engineering* **8** (2011) 117-122.
- [8] Yanagiya S.-i., Mori, A., Suzuki, Y., Miyoshi, Y., Kasuga, M., Sawada, T., Ito, K., Inoue, T., *Jpn. J. Appl. Phys.* **44** (2005) 5113-5116.
- [9] Wett, O., Engelbrecht, A., Salh R., Klassen I., Menke D., Herlach D. M., Roth, S. V., Schöpe, H. J., Competition between heterogeneous and homogeneous nucleation near a flat wall. *J. Phys.: Condens. Matter* **21** (2009) 46415-1-10.