In-situ observation of two dimensional nucleation in colloidal crystals with depletion attraction

Suxia Guo, Jun Nozawa, Haruhiko Koizumi, Junpei Okada, Satoshi Uda
Institute for Materials Research, Tohoku University
E-mail: guosuxia@imr.tohoku.ac.jp

Understanding nucleation process is critically important in fields including metallurgy, physics, biology and so on. However, Nucleation kinetics remains unclear due to the limitations of existing experimental evidence. Classical nucleation theory (CNT) cannot properly describe all aspects of the nucleation process. Colloidal crystals have been used as a good model for studying phase transition such as crystallization, glass transition, nucleation process. In this study, we focus on two-dimensional nucleation of colloidal crystals with depletion attraction, which is observed at single particle level.

Crystallization of colloid was induced by the depletion attraction, in which charged polystyrene particles and charged sodium polyacrylate polymer were mixed. 500 nm with green fluorescent polystyrene particles were used. Sodium polyacrylate was added in the solution as depletant to generate attractive interaction, and the concentration is 0.14 g/L. Nucleation process was monitored by optical microscopy. Area fraction (ϕ_{area}) is introduced to represent concentration of colloidal particles, which is defined as area occupied by particles divided by area of solution.

For the embryo with single layer, colloidal particles crystallize when the number of particles in an embryo is larger than the critical number (N*=35), while the embryos disappear if the particle number is less than the critical number (Fig. 1 I, II). However, embryos with two layers grow even if the particle number is smaller than the critical value of single layer (Fig. 1 III, IV). The critical numbers at various area fractions were obtained (Fig. 2). The shaded area represents the particle number larger than the critical value for single layer. Critical particle numbers for two layers are plotted under the shaded area. The second layer of the embryos promote nucleation.

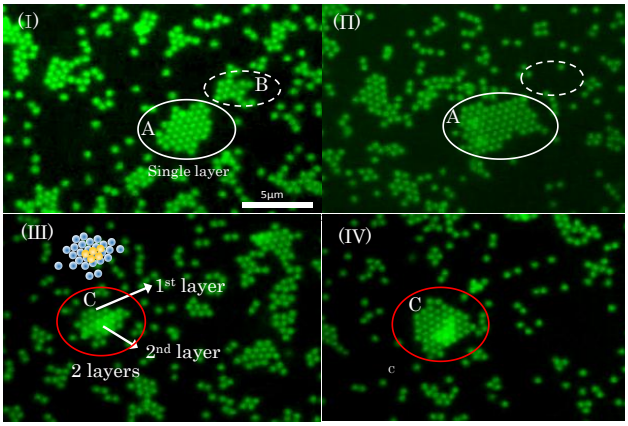

Figure 1 Snapshots of nucleation process of colloidal crystal: embryo A grow up, B disappear in images (I) and (II), embryo C with 2 layers grow up in images (III) and (IV)

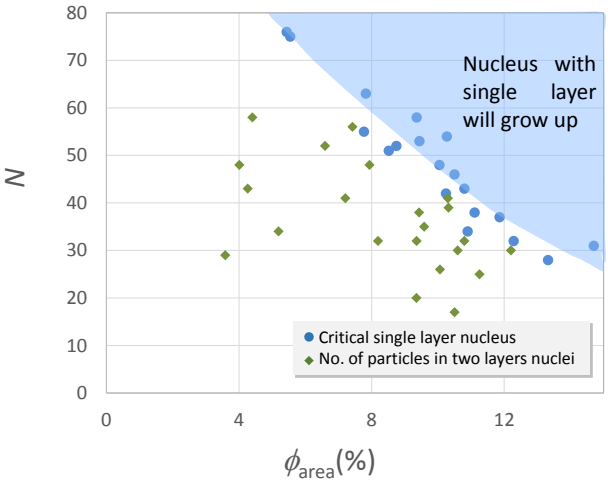

Figure 2 Maximum numbers of particles in the embryo that will disappear at different ϕ_{area} in single layer nucleus (in blue circle) and that for two layers nuclei (in green rhombus).

We explain this phenomenon by evaluating Gibbs free energy change, ΔG, of the nucleation process for single and two layers. To calculate ΔG, surface free energy and line tension are obtained based on CNT equation (which are in good agreement with the value in hard sphere model). The calculation results suggest that ΔG of two layers is smaller than that in critical single nucleus.