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The structure formation of nanoparticles during coating and drying

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1. Introduction

Thin films of ordered nanoparticles by a coating and drying process have been studied because of their potential applications such as electronic, optical, and magnetic devices. We focus on the formation mechanism of two-dimensional and patterned thin films[1)-3)] of ordered nanoparticles.

A set of numerical models for two-dimensional self-organization of nanoparticles in a liquid film during drying is developed. Numerical simulations are carried out to investigate relationship between process conditions and structures of self-organized nanoparticles. The two-dimensional Langevin equation is employed to track particles on a substrate with time. Each nanoparticle is subject to multiscale surface forces such as capillary force, contact force, electrostatic force, van der Waals force and friction drag as well as Brownian force and fluid drag as shown in Figure 1. The modeling shows that no surface force can be neglected in the self-organization process because magnitude of the surface forces strongly depends on interparticle distances and a thickness of liquid film. Three principles of two-dimensional selforganization are proposed based on unsteady behavior of nanoparticles. Isotropic ordering factor and non-dimensional boundary length are introduced to quantify structures of self-organized nanoparticles.

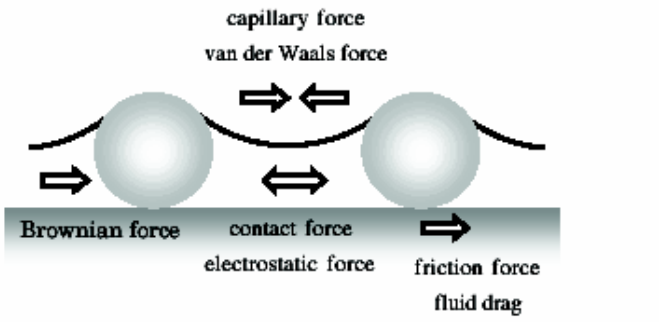

Figure 1. Various forces on two nanoparticles

2. Results

(1) Modeling[4)]

A water solution of polystyrene latex spheres with a diameter of 20 nm or 60 nm is employed, and elastic coefficients of each sphere are supposed to be identical to those of a bulk material. A temperature of the solution is 20 ºC, a contact angle on a sphere is 60º, and frictional coefficients of particle-to-particle and particle-to-substrate are 0.025. A computational time step is 0.25ps. Basic computational region is a square with a side length of 1.08 or 3.24 μm in the case of 20 nm sphere or 60 nm sphere, respectively. A periodic boundary condition that is widely used in molecular dynamics simulations is imposed on four sides. A computation is finished when values of IOF(Isotropic Ordering Factor) and NBL (Non-dimensional Boundary Length) are converged, and each *hc*, a contact height of interface, is set to be constant during a computation.

Figure 2 shows time evolutions of structure criteria, IOF and NBL for three typical cases regarding contact height of interface *hc* and zeta-potential ζ. A coverage Φ is 0.5 for these cases. Initial values of IOF and NBL are nearly equal to zero and one, respectively, because nanoparticles are non-isotropically dispersed at the start of a simulation. Figure 2(a) shows the result of $hc = 1.0r$ and $\zeta = 0$ mV. In this condition, the magnitude of capillary attractive force is much larger than those of other surface forces It is satisfactory to say that a self-organized structure is formed by a long-distance attractive force, such as capillary force. Figure 3(a) shows a principle of self-organization.

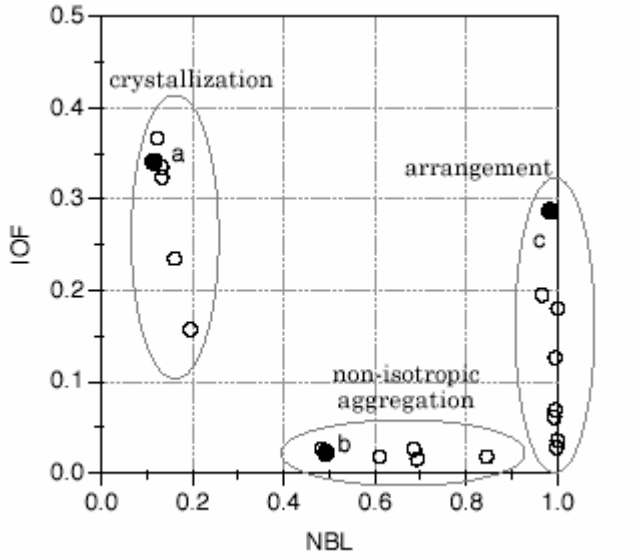

Figure 2. Three different structure points obtained from our model.

Figure 2(b) shows the result of $hc = 1.5r$ and $\zeta = 0$ mV. In this condition, magnitude of both capillary attractive force and electrostatic repulsive force are zero, so that nanoparticles

move by Brownian random force only, and two particles which have an accidental contact are expected to be attached to each other by van der Waals attractive force. This process of self-organization gradually increases the size of the structure, as is illustrated by the change of a value of NBL. On the other hand, a value of IOF is nearly equal to zero throughout the simulation. Figure 3(b) shows a principle of self-organization in this case. A randomly walking nanoparticle is attached on another nanoparticle, and it does not transfer along the nanoparticle unlike the situation of Figure 3(a), because short-distance attractive force, namely van der Waals force, cannot be exerted beyond a distance of nanoparticle size. As a result, aggregated nanoparticles form non-isotropic structures, such as chains or trees. This is the same principle of diffusion-limited aggregation of molecules in a nonequilibrium field.

Figure 2(c) shows the result of $hc = 1.5r$ and $\zeta = -100$ mV. In this condition, magnitude of electrostatic repulsive force is the largest among all surface forces except Brownian force. The magnitude of capillary attractive force was zero, so that nanoparticles are expected to form a colloidal crystal. The constant value of NBL that is nearly equal to one throughout the simulation indicates dispersed nanoparticles, and gradual increase of the value of IOF with small perturbations indicates a formation of an isotropic array. Figure 3(c) shows a principle of self-organization

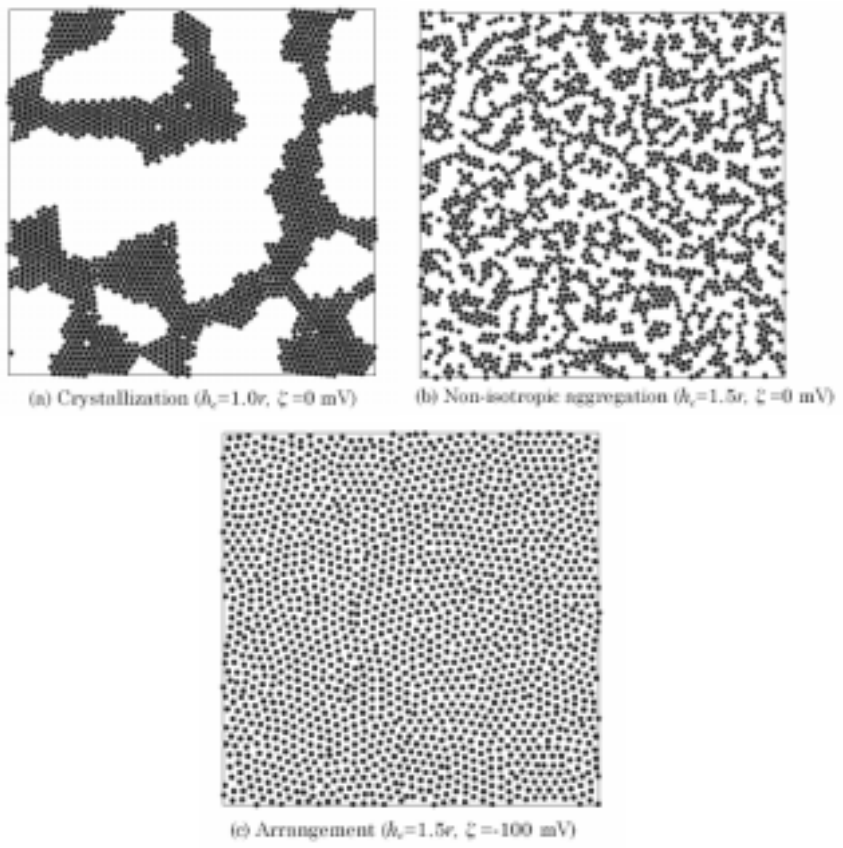

Figure 3. Final structure of self-organized nanoparticles on a substrate. Φ=0.5.

(2) Experiments

It is a key interest to obtain a highly-ordered particle thin film by using a conventional coating method. Here, we show a result of Figure 4 in terms of controlling the particle interaction by using nanoparticles. The role of silica nanoparticle is to reduce the interaction among PSL (Polystyrene Latex) particles, and results in perfectly ordered films. This result is perfectly predicted by our previous model.

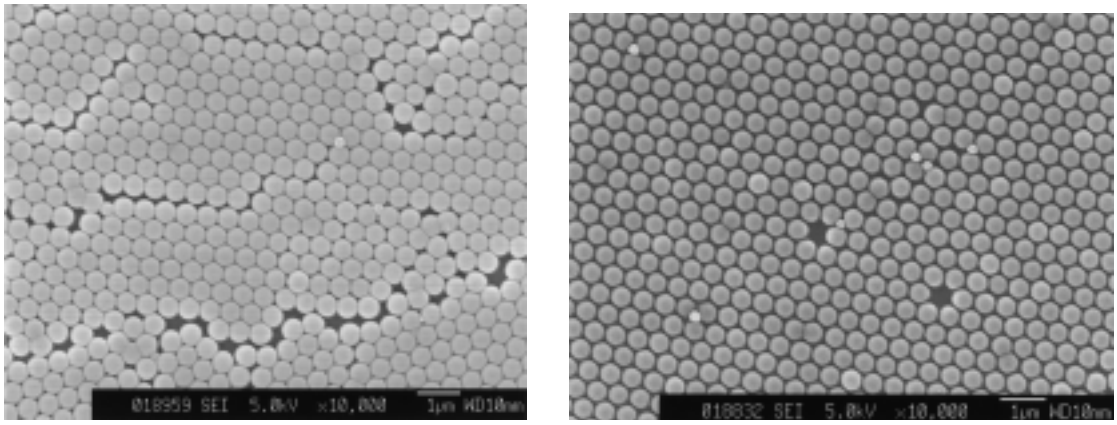

Figure 4. Highly ordered polystyrene latex particles having the average diameter of 506nm (a) without silica nanoparticles, and (b)with silica nanoparticles , 5nm.

3. Conclusions

A Two dimensional model is developed to understand the mechanism of particle ordering during drying. We also studying the ordering of particles during coating flow.

References

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