Simulation of Structure Formation and Physical Properties of Colloidal Rod-like Nanoparticles in Drying Process

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1. Introduction

Much attention is paid to thin films which consist of rod-like nanoparticles (e.g. nanorods, nanowires, and nanotubes), because of their prospective applications, such as FETs, transparent electrodes, and sensors. One of the promising techniques to produce these thin films is a coating of a nanoparticles suspension on a substrate. To control the structure of formed films, we have to care about the dispersion state of a suspension before coating as well as a drying process of solvent after coating, because the structure of formed film can be affected by both processes. Thus, comprehensive understanding of both phenomena is necessary to realize a structure-controlled colloidal thin film.

In dispersing process, rod-like nanoparticles are dispersed in a solvent. In this process, we have to control dispersion/aggregation state of nanoparticles. Colloidal stability can be discussed by the DLVO theory [1-2], in which electrostatic force and Van der Waals force are considered. Addition of surfactant is one of the widely-used techniques to make well-dispersed colloidal suspension. For anisotoropic colloids such as nanorods and nanotubes, orientational order of these colloids in a suspension is another important factor to evaluate the dispersion/aggregation state of a suspension. One theoretical understanding of orientation was given by Onsager [3], where packing entropy and orientational entropy were considered to explain the orientational phase transition. However, Onsager's theory is valid only for purely repulsive-particle system, in which no aggregation occurs. In an attractive colloidal system, orientation order of rod-like particles was observed experimentally at much lower particle volume fraction than that of predicted value by the Onsager's theory [4]. It is pointed out that this orientational ordering at lower particle volume fraction is driven by the secondary minimum of the DLVO potential [4]. While many studies have been done to examine the entropy driven orienatational ordering [5], a few reports consider the orientational ordering caused by DLVO potential. To the best of our knowledge, there is no simulation study on this orientation ordering.

In the drying process after coating of a suspension, the solvent evaporate and colloidal particles form a structure under drying. Many kinds of structures are reported so far, e.g., densely packed structures, networked structures, and fractal-like structures. In spite of many studies stated above, the formation mechanism of particle films is not clear. Sub-micron scale of colloidal particles is one of the reasons for the difficulty in direct observation of the formation dynamics of colloidal film. This prevents us to understand the formation dynamics of particles-film. In this aspect, a simulation is a powerful tool to visualize the formation dynamics of colloidal films.

We developed a simulator "SNAP-L" [6], based on the DLVO theory. Our model can calculate the dynamics of colloidal rod-like nanoparticles in a condensed suspension and even under drying. In this paper, on the basis of our

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model, orientational ordering of rod-like nanoparticles, caused by DLVO potential, will be introduced. In addition, the formation dynamics of colloidal films under drying is simulated. The relationship between orientational ordering in a suspension and the structure of formed films are discussed.

2. Simulation model

Model of a rod-like nanoparticle

As a model of rod-like nanoparticles, we employed sphere connected model, shown in Fig. 1. In this model, a rod-like nanoparticle is regarded as the serial connection of spherical segments and adjacent two segments are separated by its radius r. Additionally, each segment is mechanically bound together via two springs: axial spring and bending spring.

Equation of motion of rod-like nanoparticles

In this study, the treated radius of the segment is specifically on

Fig. 1 Model of rod-like nanoparticles

the order of 10 - 100 nm. Then individual segments in the rod-like nanoparticles would behave as a Brownian particle due to its size. Therefore, the Langevin equation with external force is adopted as the governing equation of motion for the i-th segment:

$$m_i \frac{d\mathbf{V}_i}{dt} = \mathbf{F}_i - \xi \mathbf{v}_i + \mathbf{R} \qquad (1)$$

In eq. (1), t is the time. Also, m and $\mathbf{v}_i$ are the mass and the translational velocity for the i-th segment, respectively. ξ is the Stokes' drag coefficient for a sphere. $\mathbf{R}$ is the random Brownian force. As the external force acting on the i-th segment $\mathbf{F}_i$, we employed the followings: elastic force that occurs inside an elastic rod $\mathbf{F}_i^{el}$, contact force $\mathbf{F}_i^{co}$, DLVO force (electrostatic force $\mathbf{F}_i^{e}$ and van der Waals force $\mathbf{F}_i^{w}$), and capillary force $\mathbf{F}_i^{ca}$;

$$\mathbf{F}_i = \mathbf{F}_i^{el} + \mathbf{F}_i^{co} + \mathbf{F}_i^{e} + \mathbf{F}_i^{w} + \mathbf{F}_i^{ca} \qquad (2)$$

Evaluation of the simulation results

As a result of above calculations, we can visualize the dynamical motion of rod-like nanoparticles. In addition, to quantify the state of particles, two quantities are prepared: the orientational order parameter S_θ and the non-dimensional boundary area (NBA).

First, we adopted S_θ to quantify the orientational order of rod-like nanoparticles. S_θ becomes zero and unity for the isotropic state and the completely aligned state, respectively. It is calculated as following;

$$S_\theta = \frac{1}{N} \sum_{i=1}^{N} \frac{3\cos^2 \theta_i - 1}{2} \qquad (3)$$

N is the total number of rods and θ_i is the angle between the director and the axis of the i-th rod.

Second, the NBA is introduced to quantify the mean boundary area of aggregates. NBA is unity in a fully dispersed state and decreases as the aggregation proceeds. It is defined by the coordination number of segment:

$$NBA = \frac{1}{C_{max} N_s} \sum_{k=0}^{C_{max}} (C_{max} - k) N_s(k) \qquad (4)$$

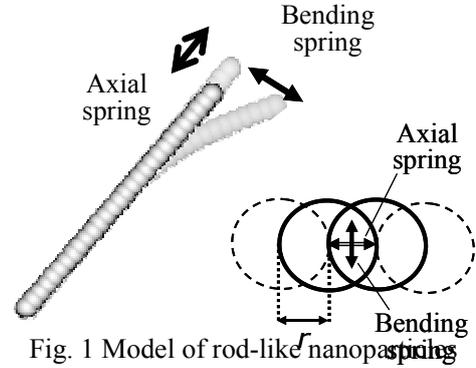N_s is the total number of segments. $N_s(k)$ is the number of segments with the coordination number of k. C_{max} is the maximum coordination number of the segment.

3. Results and discussion

Dispersing process

In DLVO theory, as the magnitude of ζ potential increases, colloidal stability becomes more stable. In the present study, we first examined this effect under different ionic strength.

As a model material, let us suppose here nanoparticles of zinc oxide dispersed in ethanol. The diameter and the aspect ratio of the particle is 10 nm and 15, respectively. The volume fraction of the particle is 0.03, in which orientational ordering doesn't occur by the prediction of the Onsager's theory. Two Ionic strengths are chosen: 1.0×10^{-4} [mol/l] (typically low) and 1.0×10^{-2} [mol/l] (typically high). The ζ potential is varied from 0 mV to 50 mV. The time step is 2.0 ps, and the total simulation time is 1.0 μs.

Particles changed their state from aggregated to dispersed, as the ζ potential increases in both regions. This trend agrees with DLVO theory. However, in dispersed state, there appeared a spontaneous difference by ionic strength: while particles are dispersed randomly in low ionic strength, particles are dispersed with orientational order in high ionic strength (Fig. 2). This difference can be expressed clearly by S_θ and NBA. In Fig. 2 (a), NBA = 1.0 and S_θ = 0.21, while in (b), though NBA is the same value as (a), 1.0, S_θ = 0.84.

Fig. 2 Dispersed state of rod-like nanoparticles at (a) low ionic strength (1.0×10^{-4} mol/l), and (b) high ionic strength (1.0×10^{-2} mol/l)

To investtigate the cause of this difference, we calculated the DLVO potential of each state (Fig. 3). At low ionic strength, electrostatic force is dominant, thus the DLVO potential is purely repulsive. At high ionic strength, however, the DLVO potential has a deep secondary minimum, because the Van der Waals force is also dominant. This secondary minimum could trap the particles, and then such orientational ordering had occurred. This is also supported by the fact that, the average particle distance in Fig. 2 (b) is almost the same as the distance at which DLVO potential reaches the secondly minimum in Fig. 3.

Fig. 3 DLVO potential as a function of surface distance. The dotted line is 1.0×10^{-4} mol/l and the solid line is 1.0×10^{-2} mol/l, respectively.

Drying process

In this section, we will discuss about the film formation of colloidal rod-like nanoparticles during drying. In our drying simulation, a suspension experiences an evaporation of a solvent at constant rate, until all the solvent is removed. As the initial condition, two results in Fig. 2 (a) and 2 (b) were chosen. Height of the initial suspension is 330 nm and the evaporation rate is 0.01 m/s.
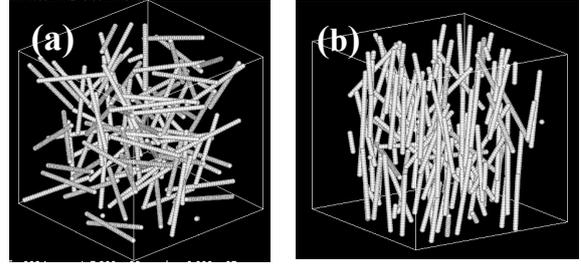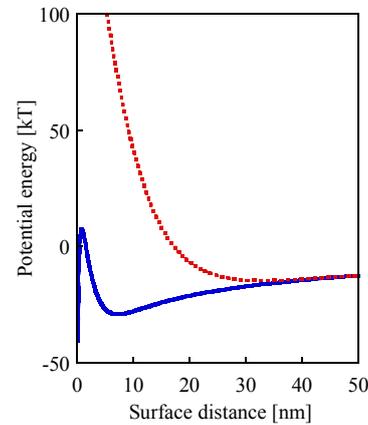
From the isotropic suspension (Fig. 2 (a)), randomly networked structure was formed. On the other hand, from the orientationaly orderd suspension (Fig. 2 (b)), a densely packed and aligned structure was formed. Each structure is shown in Fig. 4.
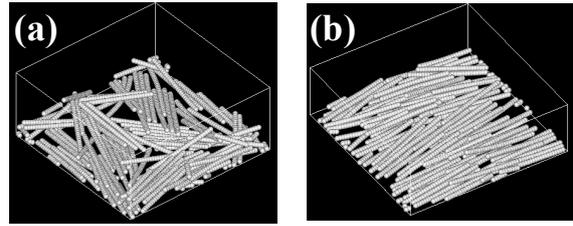
Fig. 5 is the time profile of S_θ and NBA during drying of the isotropic suspension. Until the height of interface reached about 20 nm, S_θ and NBA changed gradually. However, after the point, rapid change had occurred: S_θ leaped drastically, while NBA first quickly dropped and after bumped again. This change is due to the strong capillary force, and 20 nm is the point at which the interface begins to pass through particles.
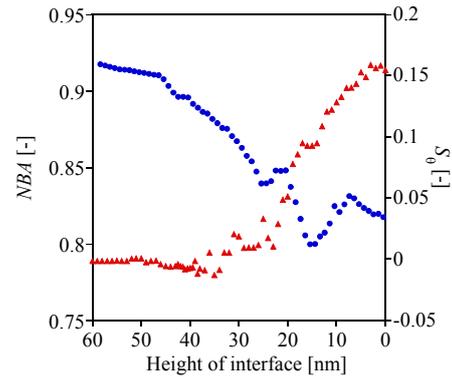
The capillary force dramatically changes the structure of the film, and this change suddenly stops when the evaporation is completed. That means the final structure of the film doesn't reach equilibrium state. If the change reaches equilibrium state, the structure of the two films might be more resembled. But because of the nonequilibrium nature of the drying process, the final structure of the film is strongly depended on the initial state of the suspension.

Fig. 4 Structure of the film formed from (a) the isotropic suspension, and (b) the orientationaly ordered suspension

Fig. 5 The time evolution of S_θ and *NBA*. ▲: S_θ, ●: *NBA*

4. Conclusion

We simulated the orientational ordering of rod-like nanoparticles, driven by DLVO potential. By changing ionic strength, we successfully simulated both isotropic and orientationaly ordered suspensions. In addition, the formation of colloidal films during drying was also simulated. The final structure of the film is strongly depended on the initial state of the suspension, because of the nonequilibrium nature of the drying process. It can be said that controlling orientational ordering in suspension by ionic strength is one of the promising way to control the structure of thin films which consist of rod-like nanoparticles.

References

[1] B. V. Derjaguin, L. D. Landau: *Acta. Physicochim. URSS* **14** (1941) 633

[2] E. J. W. Verwey, J. T. G. Overbeek: *Theory of the Stability of the Lyophobic Colloids* (Elsevier, Amsterdam, 1948)

[3] L. Onsager: *Ann. N. Y. Acid. Sci* **51** (1949) 627

[4] H. Maeda, Y. Maeda: *Phy. Rev. Let.* **90** (2003) 018303

[5] S. Fraden and G Maret: *Phys. Rev. E* **48** (1993) 2816

[6] O. Koike, S. Ohta, M. Fujita and Y. Yamaguchi: *Jpn. J. Appl. Phys* (Accepted for publication)