Flow and Drying Simulation of Nanoparticle Suspension on Substrate

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Introduction

During a continuous coating-drying process of nanoparticles suspension on a substrate, the nanoparticles are subject to a shear flow and a drying of the solvent, as shown in Fig. 1. Then shear-induced and drying-induced structure formation of the nanoparticles can take place on the substrate. After the coating-drying process, the structure of nanoparticles on the substrate develops a variety of practical functions. In order to control a final structure of nanoparticles, it is necessary to elucidate the mechanism of shear-induced and drying-induced structure formations.

Fig. 1   Schematic picture of continuous coating-drying process of nanoparticles suspension on substrate.

Numerical simulation is a powerful tool to elucidate the mechanism, because the dynamics of each nanoparticle is visualized with time. The shear-induced structure formation of the nanoparticles is characterized by coating Péclet number $Pe_c = cd^2/Dh$, where c is coating speed, d is the diameter of nanoparticle, D is self-diffusion coefficient of the nanoparticle and h is wet film thickness of the suspension. The drying-induced structure formation of the nanoparticles is characterized by drying Péclet number $Pe_d = eh/D$, where e is drying speed of the wet film. If the ratio of Péclet numbers Pe_c/Pe_d is close to 0, the effect of shear-induced structure formation is negligible compared with the effect of drying-induced structure formation. On the other hand, the ratio of Péclet numbers Pe_c/Pe_d is much larger than 1, one can independently take into account of the both effects. In other words, the shear-induced structure formation is followed by the drying-induced structure formation. The authors have ever performed independently the simulation of shear-induced structure formation [1] and the simulation of drying-induced structure formation [2]. The ratio of Péclet numbers is rewritten as $Pe_c/Pe_d = c/e \cdot (d/h)^2$. The ratio
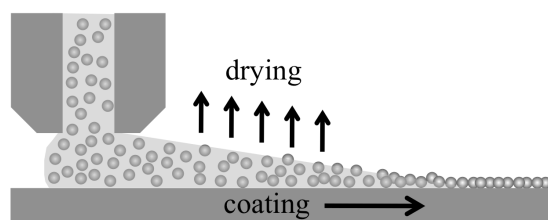
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can be close to 1 because c/e is normally larger than 1 and d/h is less than 1. In the case of $Pe_c/Pe_d \sim 1$, both the shear-induced structure formation and the drying-induced structure formation are expected to take place simultaneously. Therefore a flow and drying simulation of nanoparticles suspension on the substrate is required to elucidate the mechanism of structure formation of the nanoparticles during the coating-drying process. This paper presents a modeling for the flow and drying simulation of nanoparticles suspension on a substrate with a typical simulation result.

Simulation method

Three types of modeling are required to perform the flow and drying simulation of nanoparticles suspension. That is, a mesoscale hydrodynamic modeling of suspension, a two-phase flow modeling including gas and liquid, and a non-hydrodynamic interaction modeling between the nanoparticles. Firstly, the mesoscale hydrodynamic modeling represents the treatment of hydrodynamic interaction between the nanoparticles to satisfy the fluctuation-dissipation theorem [3]. The present mesoscale hydrodynamic model is an off-lattice-on-lattice hybrid model based on the fluctuating Navier-Stokes equation [4]. The equation naturally reproduces multi-body Brownian motion of the nanoparticles that satisfies the fluctuation-dissipation theorem. A fictitious domain method is employed to couple the off-lattice dynamics of the nanoparticles with the on-lattice dynamics of the solvent. Secondly, the present gas-liquid two-phase flow model is an one-fluid model. The one-fluid model employs a unified hydrodynamic equation for gas phase and liquid phase. The both phases are distinguished by volume-of-fluid (VOF) function on the lattice. The VOF function is transported by the fluid velocity and generated by the phase transition. The unified hydrodynamic equation incorporates a surface tension that is expressed by continuum surface force (CSF) model. Finally, the present non-hydrodynamic interaction model between the nanoparticles consists of contact interaction, van der Waals interaction, electrostatic interaction and capillary interaction. These interactions are given by the analytical two-body interactions and incorporated into the off-lattice motion equation of nanoparticle as external forces or torque.

Using the above models, the free-surface flow of the nanoparticles suspension on the moving substrate just after a coater lip is simulated in the present study. The simulation domain is a rectangular parallelepiped on the substrate. The substrate moves in-plane at the specified coating speed. The flow out condition is imposed on the top boundary. The periodic flow condition is imposed on the side boundaries. The initial thickness of the wet film of the suspension is $h = 300$ nm. The diameter of spherical nanoparticles is $d = 100$ nm. The zeta potential of the nanoparticles and the substrate is -50 mV. The frictional coefficient between the nanoparticles and that between the nanoparticles and the substrate are the same as $\mu = 0.1$. Other physical and chemical properties of the nanoparticles and the solvent are given by the same values as silica and water in normal temperature, respectively. The initial concentration of the nanoparticles is 14.3 vol% that corresponds to surface coverage on the substrate of 0.7. The coating speed is $c = 12.9$ cm/s, and the drying speed is $e = 1$ cm/s. Then the coating Péclet number is $Pe_c = 1,000$,

and the drying Péclet number is $Pe_d = 700$. Thus, the ratio of Péclet numbers is $Pe_c/Pe_d = 1.43$. The discretized time step is 0.05 ns, and the total simulation time is 30 μs. The number of computational grid points is $90 \times 90 \times 36 = 291,600$.

Simulation result and discussion

Fig. 2 shows a flow and drying simulation result of the nanoparticles suspension on the substrate. The substrate moves in the direction of arrow at the coating speed. A descending free surface is indicated by translucent grey plane in Fig. 2(a) and (b). Fig. 2 (a) shows the initial condition in which the nanoparticles are randomly dispersed in the wet film. As the free surface descends towards the substrate, some nanoparticles protrude through the free surface. The protruded nanoparticles are subject to vertical capillary force from the free surface, so that the nanoparticles also descend towards the substrate. When the film thickness becomes less than the diameter of the nanoparticles, all the nanoparticles deposit on the substrate and protrude through the free surface as shown in Fig. 2(b). The protruded nanoparticles on the substrate are subject to lateral capillary attractive force. Then the nanoparticles aggregate with one another and form a monolayer with vacancies on the substrate, because the surface coverage is 0.7. The final structure of nanoparticles on the substrate may depend on Pe_c/Pe_d. If Pe_c/Pe_d is much larger than 1, a shear-induced structure formation of the nanoparticles can take place before drying of the wet film. The shear-induced structure of nanoparticles can influence the final structure of nanoparticles on the substrate.
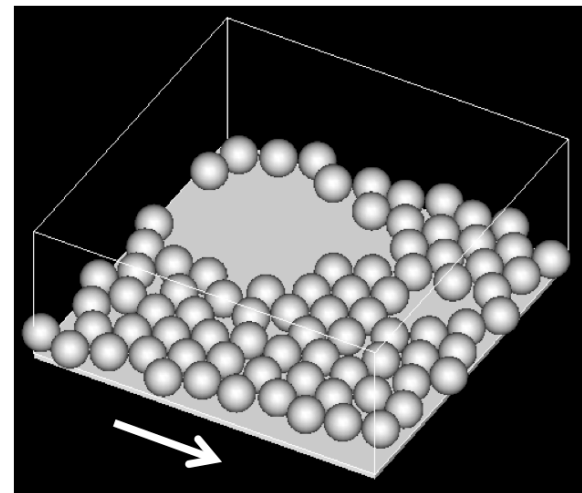
The instantaneous structure of nanoparticles can be quantitatively evaluated by nondimensional

(a) $t = 0$ μs

(b) $t = 25$ μs
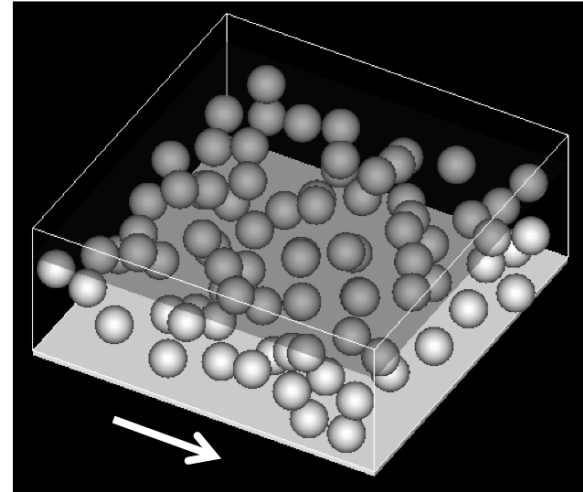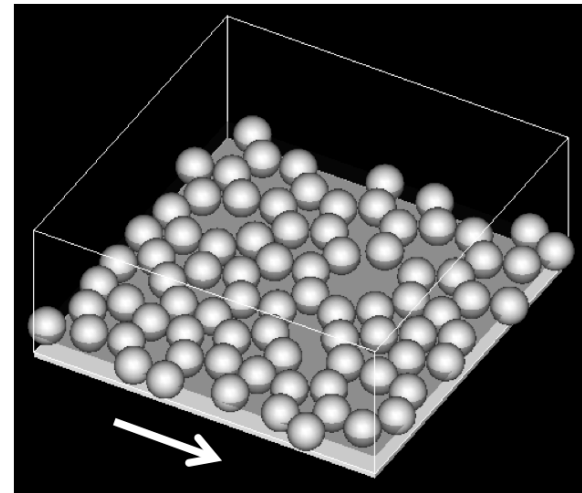
(c) $t = 30$ μs

Fig. 2 Time history of snapshots of nanoparticles on moving substrate

boundary area (NBA) [5]. The NBA represents the ratio of boundary area of aggregated particles to the summation of boundary area of each particle. The NBA becomes 1 when all particles are completely dispersed. The NBA becomes 0 when all particles are close packed. In a word, one can easily evaluate how the particles aggregate by the scalar value from 0 to 1. Fig. 3 shows time history of the NBA during the flow and drying simulation of the nanoparticles suspension on the substrate. The NBA decreases gradually with time up to $t = 25$ μs. It indicates that the nanoparticles aggregate with one another due to the shear flow and the descent of free surface. The NBA decreases suddenly at $t = 25$ μs. It indicates that the nanoparticles aggregate with one another on the substrate due to the lateral capillary attractive force

Fig. 3   Time history of NBA during flow and drying simulation

between the nanoparticles. The NBA of the final structure of nanoparticles is 0.665. On the other hand, the NBA of a close-packed hexagonal structure is 0.5. The difference between both values corresponds to vacancies in the planar structure of nanoparticles.
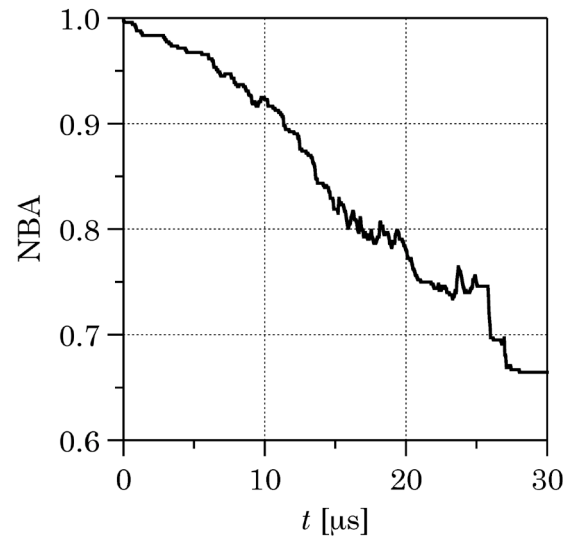

Conclusion

This paper has presented a modeling for a flow and drying simulation of nanoparticles suspension on a substrate. A typical simulation has shown a visualization of the nanoparticles dynamics during a continuous coating-drying process. The structure formation of nanoparticles has been quantitatively evaluated with time. The present simulation model will be a novel tool to elucidate the mechanism of the structure formation of nanoparticles during a coating-drying process, because the simulation model can be applied to a system of $Pe_c/Pe_d \sim 1$ in which a shear-induced structure formation and a drying-induced structure formation coexist.

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