

Self-organization Simulation of Colloidal Nanoparticles with Strong Hydrodynamic Interactions

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In a coating process of colloidal nanoparticles, self-organization of nanoparticles takes place due to interactions between nanoparticles and interactions between nanoparticles and a solvent. Fig. 1 shows a schematic picture of colloidal nanoparticles in a gap between a blade and a substrate in a coating process. The colloidal nanoparticles in the gap are subject to contact interaction, electrostatic interaction and van der Waals interaction with other nanoparticles. In addition, the nanoparticles are subject to strong hydrodynamic interactions with the solvent in a shear flow field. It is very important to clarify the mechanism of self-organization of nanoparticles in order to control coating results. However, it is difficult to investigate dynamics of the nanoparticles by existing experimental methods. On the other hand, numerical simulation

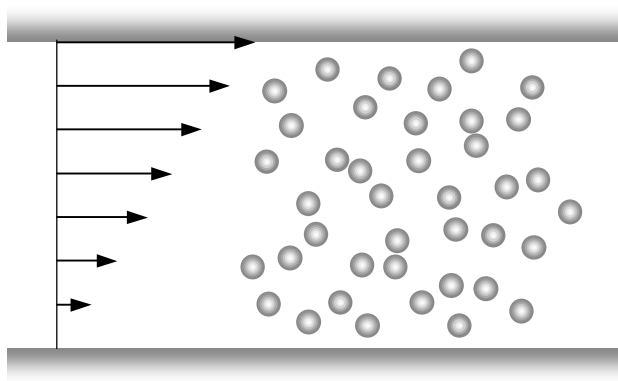


Fig.1 Colloidal nanoparticles in a gap between a blade and a substrate in a coating process

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is expected to be an effective methodology, because the motion of nanoparticles is visualized with time and the structure of nanoparticles can be quantitatively evaluated. We need a numerical model that is able to count accurately strong hydrodynamic interactions in a concentrated colloid. We here present an integrated high-resolution simulation method that can treat all interactions described before. The motion of nanoparticles and the motion of a solvent are solved simultaneously in a Lagrangian manner and an Eulerian manner, respectively. Viscoelastic contact force, electrostatic force and van der Waals force exerted between nanoparticles are included in the motion equation of nanoparticles. Fluctuating force yielding Brownian motion of nanoparticles is included in the motion equation of the solvent.

The motion of solid nanoparticles is solved by a Lagrangian scheme and the flow of solvent is solved by an Eulerian scheme on a uniform Cartesian grid. Fig. 2 shows a nanoparticle and the Cartesian grid. The diameter of a nanoparticle contains 9 grid points. Each nanoparticle is assumed to be a rigid sphere. The translational motion of the k -th nanoparticle is expressed by the Newtonian equation of motion

$$m_k \frac{\partial \mathbf{V}_k}{\partial t} = \mathbf{F}_k^c + \mathbf{F}_k^e + \mathbf{F}_k^v + \mathbf{F}_k^h, \quad (1)$$

where m_k and \mathbf{V}_k are the mass and the translational velocity vector of the nanoparticle, respectively, \mathbf{F}_k^c is solid contact force vector, \mathbf{F}_k^e is electrostatic force vector, \mathbf{F}_k^v is van der Waals force vector and \mathbf{F}_k^h is hydrodynamic force vector. The rotational motion of the k -th nanoparticle obeys the law of angular momentum conservation

$$I_k \frac{\partial \boldsymbol{\omega}_k}{\partial t} = \mathbf{T}_k^c + \mathbf{T}_k^h, \quad (2)$$

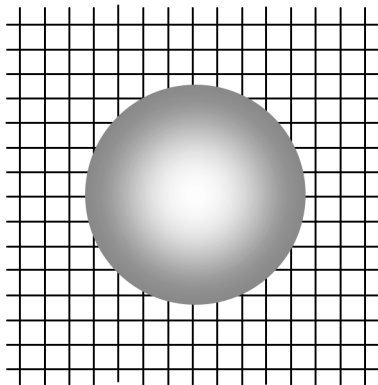


Fig.2 A nanoparticle and Cartesian grid for solving flow of solvent

where I_k and ω_k are the inertial moment and the angular velocity vector of the nanoparticle, respectively, \mathbf{T}_k^c is solid contact torque vector and \mathbf{T}_k^h is hydrodynamic torque vector. The solid contact force and torque are modeled based on a discrete element method. The method can describe a slip between nanoparticles at a contact point through frictional coefficient. The electrostatic force exerted between two spheres is treated together with the van der Waals force in the DLVO (Derjaguin-Landau-Verwey-Overbeek) theory.

The flow of the solvent is given by the fluctuating incompressible Navier-Stokes equations

$$\nabla \cdot \mathbf{u} = 0, \quad (3)$$

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 \mathbf{u} + \nabla \cdot \mathbf{s} + \mathbf{a}, \quad (4)$$

where \mathbf{u} is the fluid velocity vector, ρ is the density, p is the pressure, ν is the dynamic viscosity, \mathbf{s} is the fluctuating stress tensor and \mathbf{a} is the hydrodynamic acceleration. The hydrodynamic acceleration is given by

$$\mathbf{a} = \Phi \left(\frac{\mathbf{u}^p - \mathbf{u}}{\Delta t} + \mathbf{u} \cdot \nabla \mathbf{u} - \nu \nabla^2 \mathbf{u} - \nabla \cdot \mathbf{s} \right), \quad (5)$$

where \mathbf{u}^p is the nanoparticle velocity vector on grid points and Φ is the concentration field of nanoparticles. The value of Φ is 1 inside nanoparticles and 0 outside nanoparticles. The pressure inside nanoparticles is set to 0 as

$$p = 0 \quad : \Phi = 1, \quad (6)$$

Using Eqs. (4) - (6), velocity inside a nanoparticle at the next time step is automatically forced to the nanoparticle velocity. The hydrodynamic force in Eq. (1) and the hydrodynamic torque in Eq. (2) are obtained from the hydrodynamic acceleration through volume integrations as

$$\mathbf{F}_k^h = - \int \phi_k(\mathbf{r}) \rho \mathbf{a}(\mathbf{r}) d\mathbf{r}, \quad (7)$$

$$\mathbf{T}_k^h = - \int \phi_k(\mathbf{r}) \{ (\mathbf{r} - \mathbf{r}_k) \times \rho \mathbf{a}(\mathbf{r}) \} d\mathbf{r}, \quad (8)$$

where $\phi_k(\mathbf{r})$ is the concentration field of the k -th nanoparticle, \mathbf{r}_k is the position vector of center of the k -th nanoparticle and \mathbf{r} is position vector of grid points.

Eqs. (1) and (2) are solved by Euler explicit scheme, and the position and the rotational angle of nanoparticles are obtained by Crank-Nicolson scheme. On the other hand, Eqs. (3) and (4) are solved by the SIMPLEST algorithm. We here present two-dimensional simulation result of self-organization of colloidal nanoparticles in a shear flow field. Simulation conditions are chosen as

follows: A simulation region is a square with a side length of $1.35\ \mu\text{m}$, which is divided into 240×240 uniform Cartesian grid. Top and bottom boundaries are rigid walls, and others are periodic boundaries. The top wall moves right and the bottom wall moves left with the same speed. The shear rate is about $10^6\ 1/\text{s}$, in which Peclet number is 100. A diameter of circular nanoparticles is 50 nm, the zeta-potential of the nanoparticles is -30 mV and the frictional coefficient of particle-to-particle is 0.1. Other physical and chemical properties of the nanoparticles and the solvent are given by the same values as those of polystyrene and water in normal temperature, respectively. The coverage ratio, which is 1 if the entire simulation region is covered with hexagonally close-packed nanoparticles, is set to 0.5. Then the number of nanoparticles is 420. The total simulation time is $15\ \mu\text{s}$ and the time step for solving the equation of flow is 0.1 ns. Fig. 3 shows snapshots of colloidal nanoparticles in the shear flow field. The color of each nanoparticle represents coordinate number of the nanoparticle. The coordinate number of blue nanoparticle is 0, and that of red nanoparticle is 6. After start of the simulation, some nanoparticles aggregate with one another due to the nonuniform flow of the solvent, so that clusters of nanoparticles locally grow up. The clusters, however, maintain almost constant size after $t = 5\ \mu\text{s}$. In other words, aggregation and dispersion of the nanoparticles are in equilibrium. This is because larger clusters are subject to stronger hydrodynamic interactions and aggregated nanoparticles can disperse from the clusters. Consequently, strong hydrodynamic interactions between the nanoparticles and the solvent affect both aggregation and dispersion of colloidal nanoparticles, so that the structure of self-organized colloidal nanoparticles depends on the hydrodynamic interactions.

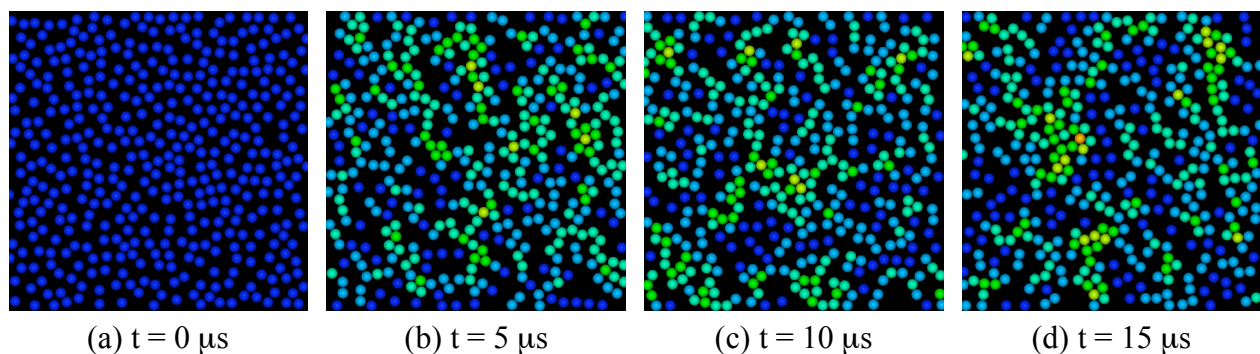


Fig.3 Snapshots of colloidal nanoparticles in the shear flow field