

Simulation of Concentrated Colloidal Nanoparticles in Simple Shear between Parallel Flat Plates

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Presented at the 14th International Coating Science and Technology Symposium,
September 7-10, 2008, Marina del Rey, California¹

Introduction

Typical nanoscale structures, such as crystals, thin films and composites that contain metal, semiconductor or polymer nanoparticles, are often fabricated by a coating-drying process of nanoparticle colloids [1, 2]. In the coating process, concentrated colloidal nanoparticles are subject to a shear, as shown in Fig.1.

The nanoparticles have an autonomous structure formation in the shear that is called self-organization. The self-organized structure of colloidal nanoparticles significantly affects the rheology of colloids. That is, shear-thickening and shear-thinning emanate associated with a shear rate [3]. It is important to control the structure of colloidal nanoparticles and the rheology of colloids in order to obtain desired properties of the nanoscale structures.

The self-organization of concentrated colloidal nanoparticles in a shear flow is caused by various interactions between nanoparticles and between nanoparticles and a solvent. The interactions are contact interaction, DLVO (Derjaguin-Landau-Verwey-Overbeek) interaction [4] and hydrodynamic interaction including thermal fluctuation of the solvent. The interactions have mesoscopic scales that lie between microscopic molecular scale and macroscopic continuum scale. Simulation of the colloidal nanoparticles is a major challenge even now when computational fluid dynamics is well developed, because typical simulation methods are based on either the microscopic or macroscopic single-phase model. Especially, concentrated systems are difficult to solve since the interactions are strongly coupled with one another.

A significant number of researchers have ever addressed mesoscopic solid-liquid two-phase modeling [5-11]. The simulation models ever proposed may have enough capability to deal with the hydrodynamic interaction between dispersed solid particles and a liquid. On the other hand, for a concentrated colloidal nanoparticles, it is also important to treat accurately the contact

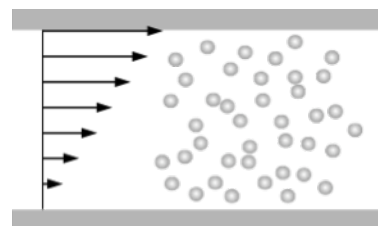


Fig. 1 Schematic picture of shear in coating process

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interaction and the DLVO interaction between the nanoparticles as well as the hydrodynamic interaction. The authors have developed an off-lattice-on-lattice hybrid simulation model [12], which has accuracy for aggregated systems where nanoparticles frequently contact with one another and has high computational efficiency for a large number of degree of freedom. The purpose of this study is to apply the simulation model on concentrated colloidal nanoparticles in a simple shear between parallel flat plates to investigate the mechanism of self-organization of nanoparticles and the rheology of colloid.

Simulation method

The present simulation method has an off-lattice–on-lattice hybrid scheme. The translational motion and the rotational motion of nanoparticles are treated by the off-lattice Newtonian dynamics. The flow of solvent is treated by the on-lattice fluctuating Navier-Stokes equation. Hydrodynamic interaction exerted on the nanoparticles can be directly resolved, because the lattice spacing is much smaller than the diameter of nanoparticle, as shown in Fig. 2. A fictitious domain (FD) method [8] is employed to couple explicitly the motion of nanoparticles with the flow of solvent. The surface of the nanoparticle is expressed by discontinuous solid-liquid boundary to calculate accurately the contact interaction and the DLVO interaction between the nanoparticles. At the same time, the surface of the nanoparticle is expressed by continuous solid-liquid boundary to calculate efficiently hydrodynamic interaction. The contact interaction is evaluated according to the Voigt model [13], in which both elastic and viscous repulsions are included in the tangential direction as well as in the normal direction. The fluctuating Navier-Stokes equation is discretized to a finite volume expression that is solved by the SIMPLEST (semi-implicit method for pressure-linked equations shortened) [14] that is an efficient variant of the SIMPLE [15]. The pressure in the particles is fixed to zero when the entire pressure field is solved. The present model includes all crucial forces and torques, such as contact force and torque, van der Waals force, electrostatic force, and hydrodynamic force and torque including thermal fluctuation of the solvent. The mathematical expressions and the numerical algorithm are described in Ref. [12] in detail.

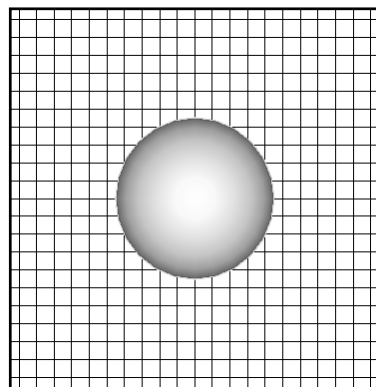


Fig. 2 Nanoparticle on computational lattice

Simulation condition

A rectangular parallelepiped simulation domain is shown in Fig. 3. The top and bottom boundaries of the domain are flat plates that move at a same speed in opposite directions each other, so that a simple shear emanates in the simulation domain. The periodic boundary condition is imposed in other directions. The simulation domain contain identical spherical nanoparticles with the diameter of $2a = 50$ nm. The zeta potential of nanoparticles and the flat plates is ζ

= -40 mV. The frictional coefficient between the nanoparticles and that between the nanoparticles and the flat plates 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 polystyrene and water in normal temperature, respectively. Simulations are carried out at a shear rate of $\gamma = 1.37 \times 10^7$ 1/s. Then Péclet number $Pe = \gamma a^2/D$ becomes 1000, where $D = 6\pi\mu/k_B T$ is coefficient of self-diffusion of a nanoparticle. The volume fraction of nanoparticles is varied from $\phi = 0.1$ to $\phi = 0.3$. The discretized time step is 0.1 ns, and the total simulation time is 3 μ s.

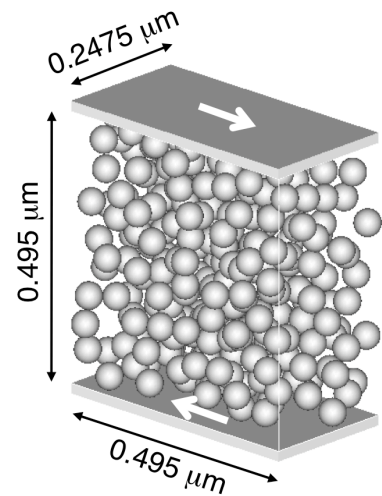


Fig. 3 Simulation domain and nanoparticles ($\phi = 0.3$)

Results and discussion

Fig. 4 shows distribution of the nanoparticles and contour of magnitude of the fluid velocity in the central plane of the simulation domain at $t = 3 \mu$ s. The colloidal nanoparticles aggregate and phase separations take place in every simulation. This may be due to that the energy of relative motion of the nanoparticles overcomes the repulsive potential barriers between the nanoparticles. At all volume fractions, the aggregates of nanoparticles exist around the center in the direction of shear, and the shear flow is localized in the gap between the aggregates and the walls. In a word, the nanoparticles are self-organized due to the externally applied shear. The structures of nanoparticles can be quantitatively evaluated by nondimensional boundary area (NBA), which is three-dimensional extension of nondimensional boundary length (NBL) [12]. The NBA represents the ratio of boundary area of aggregated nanoparticles to the summation of boundary area of each nanoparticle. The NBA becomes 1 when all nanoparticles are completely dispersed. The NBA becomes 0 when all nanoparticles are close packed. Figure 5 shows time history of NBA for different volume fractions. The NBAs for every simulation decrease with time and reach almost the same value. Namely, the volume fraction does not affect the structures of nanoparticles but affect the time during which the structures are formed.

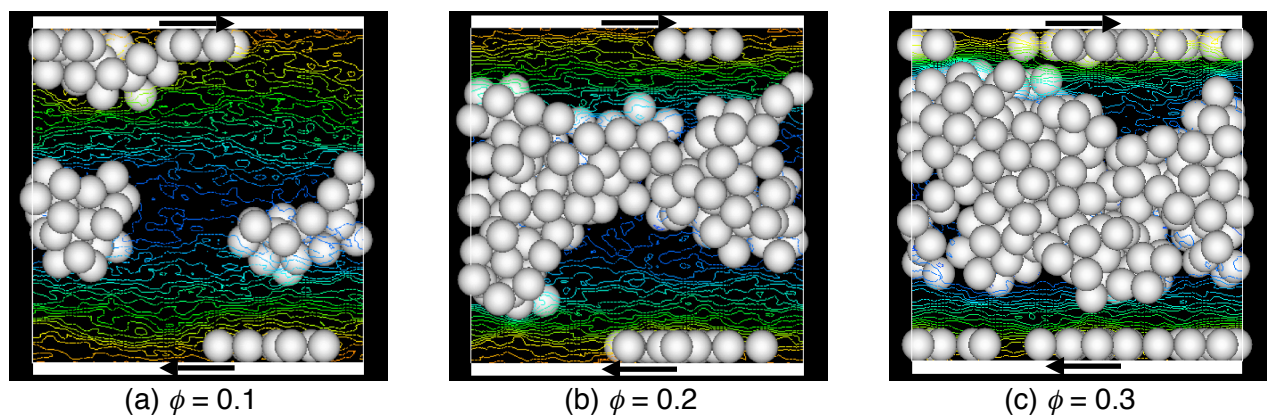


Fig. 4 Snapshots of simulation results at $t = 3 \mu$ s

Figure 6 shows time history of specific viscosity of the colloid. The specific viscosity is the ratio of viscosity of the colloid to the viscosity of solvent. The viscosity of colloid is calculated from the tangential stress that is exerted on the walls. Although the viscosity of colloid increases compared to the viscosity of solvent in every simulation, the viscosity gradually decreases with time. This may be due to that the aggregates of nanoparticles change their shapes to decrease the fluid drag exerted on them. After a long enough length of simulation time, the viscosity is expected to reach a quasi-steady value that is a function of volume fraction.

Conclusion

A simulation of concentrated colloidal nanoparticles in a simple shear between parallel flat plates has been carried out. The simulation result shows that the colloidal nanoparticles aggregate and the phase separation take place at a high shear rate ($Pe = 1000$) regardless of a volume fraction of nanoparticles. The viscosity of colloid has been calculated as a function of volume fraction.

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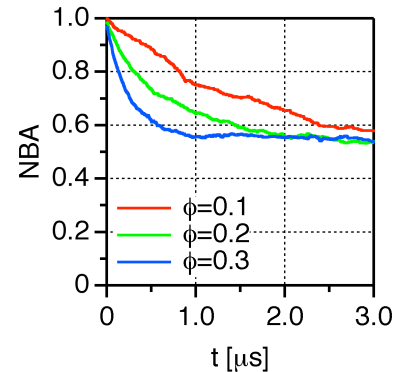


Fig. 5 Time history of NBA

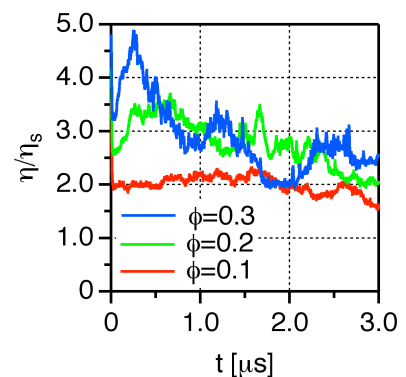


Fig. 6 Time history of specific viscosity