

## Simulation Method of Colloidal Suspensions with Hydrodynamic Interactions: Fluid Particle Dynamics

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We develop a new simulation method of colloidal suspensions, which we call a “fluid particle dynamics” (FPD) method. This FPD method, which treats a colloid as a fluid particle, removes the difficulties stemming from a solid-fluid boundary condition in the treatment of hydrodynamic interactions between the particles. The importance of interparticle hydrodynamic interactions in the aggregation process of colloidal particles is demonstrated as an example. This method can be applied to a wide range of problems in colloidal science.

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The dynamic behavior of colloidal suspensions is quite important from both scientific and industrial viewpoints [1,2]. It includes many fundamental problems, e.g., rheological behavior of colloidal systems under shear fields and the kinetics of colloidal aggregation, phase separation, gel formation, and crystallization. If we try to attack these problems either theoretically or numerically, the most difficult problem arises from hydrodynamic interactions between solid particles. The nonlocal nature of hydrodynamic interactions is a key physical factor that makes this problem so rich, but at the same time so difficult. It is known that for the creeping-flow regime, truncating the hydrodynamic interactions beyond some critical distance causes serious errors because of the intrinsically long-range nature of the interactions. This situation is physically very similar to the problem of interacting charged particles, where spherical truncation of the Coulomb interaction between ions leads to large errors. If we explicitly treat a solid-fluid boundary of a colloid particle, thus, enormous calculations are required. A number of approximation methods are proposed to reduce the calculation time with keeping the important effects of hydrodynamic interactions [3–9]. These considerable improvements of methods and recent advance of computers now make numerical simulations powerful and popular means to study the dynamics of suspensions. However, hydrodynamic interactions between particles are still serious obstacles for our understanding of the dynamics of colloidal suspensions. Thus, one of the main goals of colloidal science is to reveal the physical nature of long-range interparticle hydrodynamic interactions in a dense particle system.

There are a number of interesting problems, where interparticle hydrodynamic interactions may play crucial roles. For example, colloidal phase separation, aggregation, and gel formation have recently attracted considerable attention. Phase separation in such a system has been found to have many unusual features including a long-lived transient gel state [10–12]. For a deep quench, for example, the initial growth of the concentration fluctuations is fol-

lowed by the formation of a transient gel, and the coarsening process apparently stops for a while. This transient gel state lasts for a long time, and then the gel eventually collapses under gravity. Phase separation of emulsion [13–15] also has similar features. Since these phenomena occur in dense colloidal suspensions, hydrodynamic interactions should be quite important.

Many simulation studies have so far been performed to understand these interesting, but mysterious phenomena [15–18]. In all these studies, the so-called Brownian dynamics simulations are employed to save the computation time. The hydrodynamics is free draining there and thus hydrodynamic interactions between particles are completely ignored. However, there is a high possibility that hydrodynamic interactions between the particles play a crucial role in the structural formation during aggregation or phase separation. This is indeed the case, as demonstrated below. To our knowledge, there are no simulations with interparticle hydrodynamic interactions on this problem. This may be largely due to the difficulty in dealing with many-body hydrodynamic interactions in a dense colloidal suspension. So an efficient simulation method properly handling hydrodynamic interactions in a colloidal suspension is highly desirable. Since the similar behavior is also observed for a suspension of rodlike colloidal particles [19], the applicability of the method to particles with an arbitrary shape is also desirable.

In previous simulations, colloidal suspensions were usually treated as a mixture of solid particles and a simple liquid. This is quite natural since it reflects the reality. However, this type of approach inevitably suffers from the solid-fluid boundary conditions on the surface of colloidal particles, which make simulations very complicated and accompany the problem of the singularity associated with the squeezed flow [6]. In this Letter, we demonstrate a new simulation method, which is essentially different from conventional ones in the point that we view colloidal suspensions as a mixture of viscous undeformable fluid particles and a nonviscous simple liquid, instead of treating colloids

as solid particles. We call this new method a “fluid particle dynamics” (FPD) method.

First we explain our FPD method. This method is based on a new hybrid model, which combines a lattice simulation for continuous fields and an off-lattice simulation for particles. We use  $\mathbf{r}$  for an on-lattice site, while  $\mathbf{r}_i$  for an off-lattice position of particle  $i$ . A colloidal suspension is treated as a completely immiscible fluid mixture, in which undeformable but viscous fluid particles with the viscosity  $\eta_c$  are suspended in a liquid component with the viscosity  $\eta_s$ . In the limit of  $\eta_c/\eta_s \rightarrow \infty$ , fluid particles can be regarded as solid ones. Thus, this viscosity ratio  $R (= \eta_c/\eta_s)$  is a measure of the accuracy of our approximation. A particle whose center of mass is located at  $\mathbf{r}_i$  is represented by concentration fields

$$\phi_i(\mathbf{r}) = [\tanh\{(a - |\mathbf{r} - \mathbf{r}_i|)/\xi\} + 1]/2, \quad (1)$$

where  $a$  is the radius of a particle and  $\xi$  is the interface thickness. Then the spatial distribution of the viscosity is given by  $\eta(\mathbf{r}) = \eta_s + \sum_i^N \Delta\eta \phi_i(\mathbf{r})$ , where  $\Delta\eta$  is the viscosity difference between the liquid and colloids. Note that  $\eta_c = \eta_s + \Delta\eta$ . The summation is taken over all the particles ( $N$  particles) in the simulation volume. For our simulations we use a Lennard-Jones potential of short-range attraction,  $V(r)$ , as an interparticle potential between particles separated by the distance  $r$ , although we can in principle use any potential shape:

$$V(r) = k \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (2)$$

where  $k$  is the strength of the potential and  $\sigma$  is the range of interaction. The force acting on particle  $i$ , whose center of mass is located at  $\mathbf{r}_i$ , is then determined as  $\mathbf{F}_i = -\partial \sum_{j \neq i}^N V(|\mathbf{r}_i - \mathbf{r}_j|)/\partial \mathbf{r}_i$ . Then the continuous force fields  $\mathbf{F}(\mathbf{r})$  can be obtained as  $\mathbf{F}(\mathbf{r}) = \sum_i^N \mathbf{F}_i \phi_i(\mathbf{r})$ . The equation of motion is thus given by the Navier-Stokes equation

$$\rho \frac{D}{Dt} \mathbf{v} = \mathbf{F} - \nabla p + \nabla \cdot [\eta \{ \nabla \mathbf{v} + (\nabla \mathbf{v})^t \}] + \boldsymbol{\zeta}, \quad (3)$$

where  $\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla$ ,  $\rho$  is the density, and  $\boldsymbol{\zeta}$  is the thermal force noise. Pressure  $p$  is determined to satisfy the incompressibility condition. In our simulations we ignore the nonlinear term  $\rho \mathbf{v} \cdot \nabla \mathbf{v}$  and the force noise term  $\boldsymbol{\zeta}$  just for simplicity. We also assume that the density of colloidal particles is the same as that of a liquid, but the density difference and the resulting effects of gravity can be straightforwardly included in the above equation.

Initially particles are distributed in space with avoiding the overlap with them. Using the continuous force fields  $\mathbf{F}$  determined by the particle distribution, we calculate the velocity fields by solving Eq. (3) under the incompressibility condition  $\nabla \cdot \mathbf{v} = 0$ : The velocity fields at  $t + \Delta t$  are incremented by

$$\rho \Delta \mathbf{v} = [\mathbf{F} - \nabla p + \nabla \cdot \{ \eta (\nabla \mathbf{v} + (\nabla \mathbf{v})^t) \}] \Delta t, \quad (4)$$

where  $\Delta t$  is a time step ( $\Delta t = 0.01$ ). Here  $\mathbf{F} - \nabla p + \nabla \cdot [\eta (\nabla \mathbf{v} + (\nabla \mathbf{v})^t)]$  is calculated by an inverse Fourier transformation of  $\mathbf{T}_q \cdot [\mathbf{F} + \nabla \cdot \{ \eta (\nabla \mathbf{v} + (\nabla \mathbf{v})^t) \}]_q$ . Here  $\mathbf{T}_q = \mathbf{I} - \mathbf{q}\mathbf{q}/q^2$  is the operator of the transverse projection in  $q$  space, whose operation guarantees  $\nabla \cdot \mathbf{v} = 0$ . By calculating the center-of-mass velocity of each particle  $\mathbf{v}_i$  as  $\mathbf{v}_i = \int d\mathbf{r} \mathbf{v}(\mathbf{r}) \phi_i(\mathbf{r}) / \int d\mathbf{r} \phi_i(\mathbf{r})$ , we move particles by  $\Delta \mathbf{r}_i = \mathbf{v}_i \Delta t$ . This gives us a new spatial distribution of particles. Thus we obtain new  $\phi$  and  $\mathbf{v}$  fields on the lattice at a time  $t + \Delta t$ . With these fields, we solve Eq. (3) again. Then, we repeat the above procedure. In this way, we calculate the time development of both the spatial distribution of particles and continuous velocity fields in a “coupled” manner.

Our new method is hinted from model  $H$  simulations of fluid phase separation [20,21], whose hydrodynamics is also described by the Navier-Stokes equation. Note that since our simulation is based on the particle dynamics, coalescence between particles is, of course, not allowed, differently from model  $H$  simulations. This method allows us to avoid the discontinuity of flow fields at the interface. Namely, it enables us to apply the Navier-Stokes equation to our problem without suffering from solid-fluid boundary conditions. For example, the numerical singularity associated with the squeezed flow produced by two approaching particles is automatically avoided in our method because of the finiteness of  $\eta_c$ . In the limit of  $\eta_c/\eta_s \rightarrow \infty$  and large  $a$ , however, our method is expected to describe the squeezing phenomena properly. The accuracy of our approximation for colloidal suspensions increases with the increase in the viscosity ratio  $R$ . For emulsions, in which fluid particles are suspended in a simple liquid, our method should be even more realistic.

It may be worth comparing our FPD method with a few previous simulation methods. Stokesian dynamics [3] is one of the most powerful methods to properly incorporate the many-body hydrodynamic interactions. However, it suffers from the heavy calculations since calculation of the hydrodynamic interactions among  $N$  particles requires  $O(N^3)$  operations and thus limits the simulations to small  $N$  systems. Further, this method is complicated in their mathematical structures. Dissipative particle dynamics (DPD) [4] also suffers from the similar problems since it treats even the fluid component as particles. For the reasonable size ratio between colloids and fluid particles, the total number of fluid and colloid particles inevitably becomes quite large and thus the simulations require a long calculation time. In contrast, our method is numerically more efficient than these conventional methods and also physically much simpler.

First we show how the viscosity ratio  $R$  correlates with the solidlike nature of a fluid particle in FPD simulations. Figures 1(a) and 1(b) show flow fields around and inside a single particle moving with a constant velocity  $\mathbf{v}_0$  relative to the surrounding fluid, respectively, for  $R = 1$  and  $R = 50$ . The system size was  $64 \times 64$  and the particle radius was 10. The flow fields for  $R = 50$

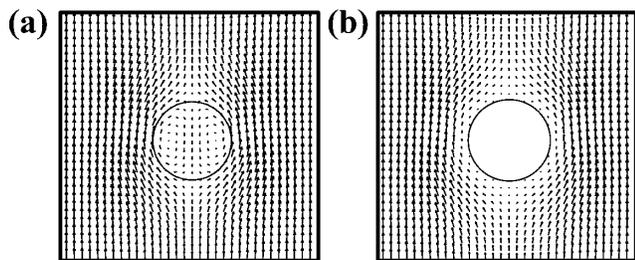


FIG. 1. Flow fields around and inside a particle simulated by a FPD method. (a)  $R = 1$ ; (b)  $R = 50$ .

are very similar to those for a solid particle. In this case, few flow fields enter inside a particle, which guarantees the validity of our new simulation method of colloidal suspensions. As shown in Fig. 2, the average strength of the residual flow fields inside a particle,  $\langle |\mathbf{v} - \mathbf{v}_0|^2 \rangle$ , monotonically decrease with increasing  $R = \eta_c/\eta_s$ ; in other words, the accuracy of the approximation increases with increasing  $R$ . Here  $\langle |\mathbf{v} - \mathbf{v}_0|^2 \rangle$  is calculated by using the relation  $\langle |\mathbf{v} - \mathbf{v}_0|^2 \rangle = \int d\mathbf{r} \mathbf{v}^2(\mathbf{r}) \phi(\mathbf{r}) / \int d\mathbf{r} \phi(\mathbf{r}) - [\int d\mathbf{r} \mathbf{v}(\mathbf{r}) \phi(\mathbf{r}) / \int d\mathbf{r} \phi(\mathbf{r})]^2$ , where  $\phi$  is the  $\phi$  field of the particle.

Next we show the results of two types of simulations, (i) FPD and (ii) Brownian-dynamics-like simulations, to compare the aggregation processes of colloidal suspensions with and without hydrodynamic interactions. (i) Two-dimensional FPD simulations are performed for a system with the size of  $128 \times 128$ . The mesh size was taken to be  $\xi$ , which was set to 1. The particle radius  $a$  was 3.5 in this unit [22] and the number of particles  $N$  was 100. Thus the volume (area) fraction  $\phi$  was 0.235. We set  $\sigma$  to the diameter of a particle ( $2a = 7$ ) and  $k$  to 1 [see Eq. (2)]. We also set  $\eta_s$  to 0.5 and  $\rho$  to 1.  $\Delta t$  was set to 0.01 to ensure the numerical stability. Periodic boundary conditions are imposed at the boundaries of the simulation volume. The results are shown in Fig. 3. (ii) Simulations without hydrodynamic interactions between particles are also performed for comparison. We solved the following equation of motion:

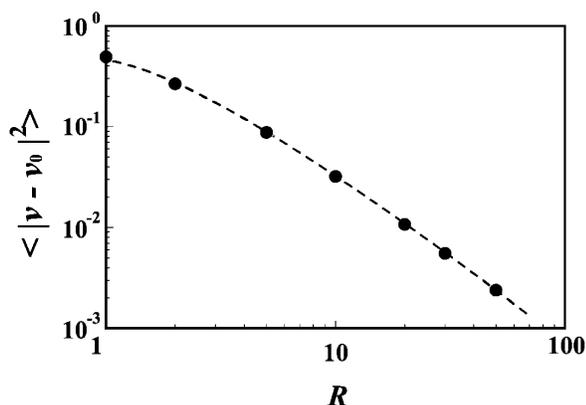


FIG. 2. Dependence of  $\langle |\mathbf{v} - \mathbf{v}_0|^2 \rangle$  (see text) upon the viscosity ratio  $R$ . The dashed curve is a guide for the eye.

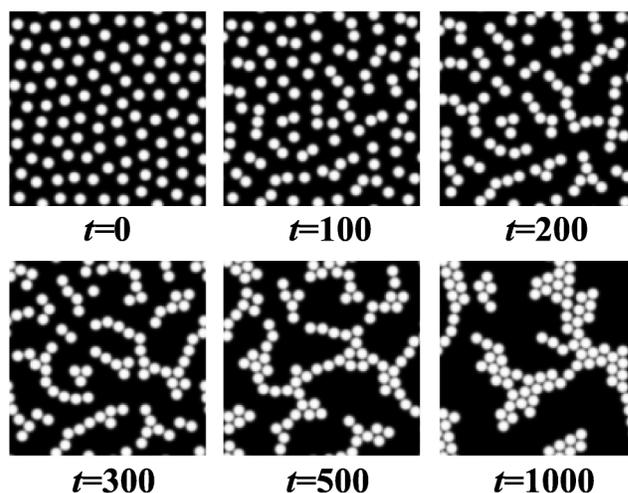


FIG. 3. A phase-separation process of colloidal suspensions simulated by the FPD method with  $R = 50$ .

$$\rho \frac{\partial}{\partial t} \mathbf{v}_i = \mathbf{F}_i - f \mathbf{v}_i. \quad (5)$$

Here  $f$  is the friction constant and set as  $f = 10^4/3$ . All the other parameters were set to the same as those of the above-described FPD simulation. The results are shown in Fig. 4. Note that in this simulation the hydrodynamics is free draining. This simulation is essentially the same as the so-called Brownian dynamics simulation except that we do not have a random force noise term in our simulations. We neglect the noise terms in both FPD and this simulation to pick up solely the effects of interparticle hydrodynamic interactions on the behavior of particle aggregation.

In Fig. 3, homogeneously distributed colloidal particles gradually form clusters with open structures after the initiation of phase separation. Effects of hydrodynamic interactions can be recognized evidently by comparing these results with those of the above-described

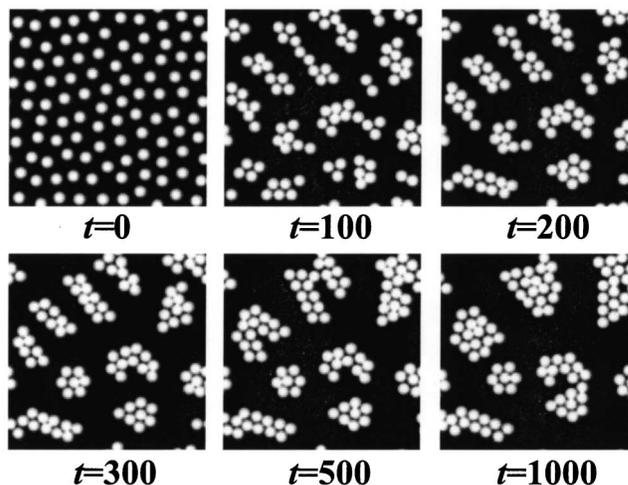


FIG. 4. A phase-separation process of colloidal suspensions simulated by the Brownian-dynamics-like method. The initial configuration of particles is the same as that of Fig. 3.

Brownian-dynamics-like simulation, which are shown in Fig. 4. Both simulations are started from the same initial particle configuration and there are no force noises. Thus, all the differences should stem solely from hydrodynamic interactions between the particles. Without hydrodynamic interactions, particles have a tendency to aggregate into a much more compact structure, as often reported in Brownian dynamics simulations [15–18]. Now it can be concluded that *the formation of clusters with “open” structures is due to interparticle hydrodynamic interactions*. This clearly demonstrates that hydrodynamic interactions crucially affect the pattern evolution and kinetics of aggregation, gel formation, and phase separation in colloidal suspensions.

Here we consider the roles of hydrodynamic interactions in the formation of chainlike open structures. To reveal physical mechanisms, let us consider the motion of a pair of particle pairs, as an example. Without hydrodynamic interactions, they approach with each other mainly by the translational motion and the rotational motion is only very weakly induced before their contact. There are also no effects of squeezed flows in this case. With hydrodynamic interactions, on the other hand, there are two mechanisms, which try to align the pair of paired particles in the same direction during their approach. One is the rotation of a particle pair toward the direction of the translational motion. This is induced by its anisotropic shape to minimize the viscous dissipation and can be explained by a simple symmetry argument. The other is due to hydrodynamic interactions between the particle pairs: The flow fields induced by the motion of a particle pair rotate the other particle pair. These mechanisms significantly increase the probability of the formation of a chainlike open structure. The hydrodynamic interactions (more specifically, squeezed-flow effects) also make the approaching speeds of particles considerably slower compared to the case without hydrodynamic interactions, which also helps the formation of chainlike structures. Our results strongly indicate that the hydrodynamic interactions between particles are quite important to understand the formation of a transient gel of colloidal particles. For example, the threshold composition required for the formation of a “transient” gel can be estimated by neither a static percolation model nor a diffusion-limited aggregation model and we must properly include hydrodynamic effects for such an estimation. The threshold volume fraction for the formation of a transient gel should be much lower for a system with hydrodynamic interactions than for that without. This point will be discussed in detail elsewhere, focusing on the unique features of phase separation behavior in colloidal suspensions [23].

In summary, we develop a new method (FPD) of colloid simulations and demonstrate its validity. The importance of interparticle hydrodynamic interactions in aggregation, gel formation, and phase separation of colloidal suspensions is clearly demonstrated. Our FPD method may be a powerful tool in colloid simulations; for example, it can be applied to the studies of gravity-induced collapsing of

a transient gel and shear effects on colloidal suspensions. It is worth stressing that this method can be applied to colloidal particles of any shape without any fundamental difficulty by properly describing a shape function for the viscosity profile [see Eq. (1)] and orientation-dependent interparticle potentials.

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