

Modeling Nanosized Colloidal Particle Interactions with Brownian Dynamics Using Discrete Element Method

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ABSTRACT

We study nanosized colloidal particle interactions in solution. Brownian dynamics that mimics the effects of collisions with solvent molecules is developed and integrated into discrete element method. Equation of motion is derived so that the deterministic and stochastic parts of particle motion are solved separately. Computational strategy is developed to handle consistent movement of Brownian cluster comprising agglomerated particles. An intensive geometric check is developed to prevent unrealistic overlapping, possibly caused by random motion from Brownian dynamics. The nanosized SiC particles in electro-plating solution are modeled. The simulation results indicate that Brownian dynamics effects primarily dominate the agglomeration processes of colloids.

Keywords: Brownian dynamics, DEM, DLVO, Colloid, Agglomeration.

1 INTRODUCTION

Discrete element method (DEM) has been developed in an integrated software system to study ceramic particle suspension and colloidal forming process recently [1]. Particle interactions such as van der Waals attraction, electrical double-layer repulsion, and short-range adhesive contact as well as frictional drag, rotational resistance, hydrodynamic lift, buoyancy and gravitational forces have been incorporated. In this study, Brownian dynamics that mimics the effects of collisions with solvent molecules is developed and integrated into the DEM simulation to study the agglomeration ratio and colloidal stability of nanosized SiC particles in electro-plating solution.

2 EQUATION OF MOTION

The movement of a particle in solution is governed by Newton's equation of motion where the forces include those from particle interaction, solution field and "kick" from solvent molecules. For simplicity, the different contributions to the forces are assumed to be independent to each other [2]. From the Langevin equation, the balance equation of motion for a spherical particle in suspensions can be expressed as [3]:

$$m \frac{d^2 \bar{x}}{dt^2} + 6\pi\eta a \frac{d\bar{x}}{dt} = \sum \bar{F}_{pair} + \bar{F}_{field} + \bar{F}_{Brownian} \quad (1)$$

with m the mass, η the viscosity, a the radius, and \bar{x} the central position at time t of the sphere. $\sum \bar{F}_{pair}$ comprises the force resulting from the sum of pair interactions between this and other particles in the solution. At the long range, the well-known Derjaguin-Landau-Verwey-Overbeek (DLVO) theory containing van der Waals attraction and electrostatic repulsion is used. At the short range, the Johnson-Kendall-Roberts (JKR) adhesive interaction model is applied. At very short range, the Hertz and Mindlin-Deresiewicz (HMD) mechanical contact models are used. \bar{F}_{field} is the force from the solution field acting on the particle which comprises rotational resistance, hydrodynamic lift, buoyancy and gravitational forces. The reader is referred to [1] for detailed expression and discussion of these forces.

The last term on the right hand side of Equation (1) is the fluctuating Brownian force characterizing the actuation of particles due to the solvent molecules. To simplify the calculation, we further assume that the motion caused by Brownian dynamics is independent from those by other forces. Thus, it is possible to split Equation (1) into two parts, for which the motion of particle can be expressed as:

$$m \frac{d^2 \bar{x}_1}{dt^2} + 6\pi\eta a \frac{d\bar{x}_1}{dt} = \sum \bar{F}_{pair} + \bar{F}_{field} \quad (2a)$$

$$m \frac{d^2 \bar{x}_2}{dt^2} + 6\pi\eta a \frac{d\bar{x}_2}{dt} = \bar{F}_{Brownian} \quad (2b)$$

with $\bar{x} = \bar{x}_1 + \bar{x}_2$. The \bar{x}_1 in Equation (2a) represents the deterministic part of particle motion that can be solved routinely through Euler's or predictor-corrector methods [4]. The \bar{x}_2 in Equation (2b) represents the stochastic part of particle motion due to Brownian dynamics. Following the derivations in [3], the probability $f(\Delta x, \Delta t)$ of a displacement Δx along an axis at time period Δt can be expressed as a Gaussian distribution, i.e.,

$$f(\Delta x, \Delta t) = \frac{\exp(-(\Delta x - \mu)^2 / 2\sigma^2)}{(2\pi)^{1/2} \sigma} \quad (3)$$

where $\mu = 0$ and $\sigma^2 = 2D_0\Delta t$ with $D_0 = \frac{kT}{6\pi\eta a}$. The k is Boltzmann's constant and T is the temperature. We note that two explicit assumptions are used while deriving Equation (3). The first assumption is that the Brownian forces are taken to be random in direction and magnitude and uncorrelated on the time scale of particle motion. The second assumption is that kinetic energy is partitioned equally among the three translation modes of the particle at equilibrium.

3 SIMULATION STRATEGY

Various ranges of the interaction forces between two particles with decreasing surface separation distance h are illustrated in Figure 1. Deterministic interactions modeled by DLVO, JKR, HMD theories are plotted. Heuristic methods for Brownian motion with respect to h are also shown.

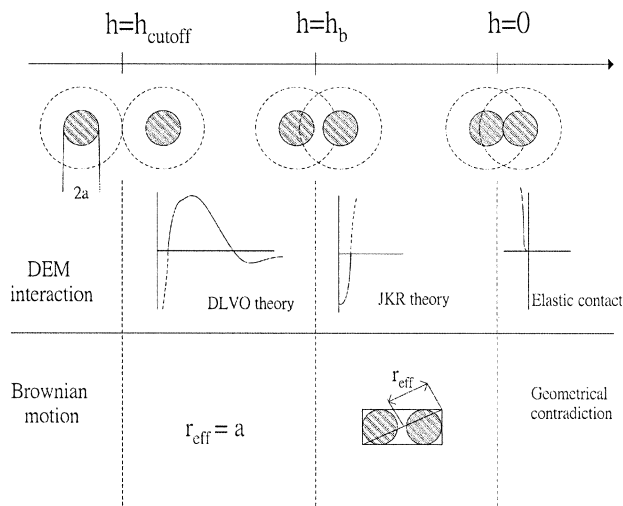


Figure 1: Various interaction theories and heuristic methods for Brownian dynamics between two particles with decreasing surface separation distance h .

A time-stepping finite difference is used to solve particle motion. The program will first initialize the position and velocity of each particle in the simulation domain. Based on the equation of motion, the total interaction forces acting on each particle will be added. Furthermore, the predicted position and velocity at next time step will be updated. The Brownian motion generator developed in this study will then impose a random displacement for each particle before moving to the next time step. The scenario of the DEM program with Brownian motion simulation is shown in Figure 2.

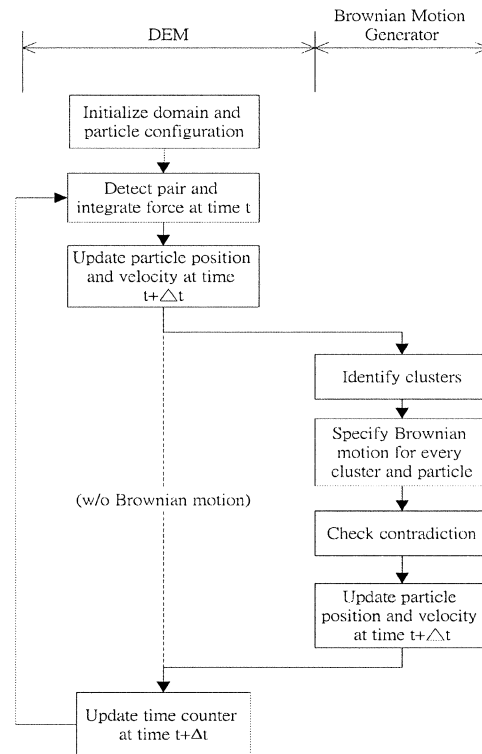


Figure 2: Scenario of DEM with Brownian motion.

3.1 Formation of clusters

Particles tend to agglomerate in solution. To impose the Brownian motion properly to particles, clusters with a group of particles need to be identified. As shown in Figure 1, two or more particles when their surface separation h is below a specific distance h_b are assumed to form a cluster. All the particles in the same cluster are assumed to move in the same direction and displacement under Brownian dynamics.

The distance of balance h_b is introduced based on the DLVO potential interaction force $F_p(h)$, where $F_p(h_b) = 0$. If there is no repulsion force presented (i.e., without any electrostatic repulsion), the length of 1×10^{-6} times the particle radius is used for h_b by default. With this criterion, all the clusters at any given time t in the domain can be identified (Figure 3).

Because the Brownian motion generator is derived for spherical particle, we need to further define the effective radius and center for a cluster. Firstly, the center of mass in the same cluster is treated as the effective center, thus the base point of the random displacement can be identified (Figure 4). Secondly, to simplify the calculation, the effective radius is chosen to be equal to half of the diagonal of the rectangle containing the cluster (Figure 5).

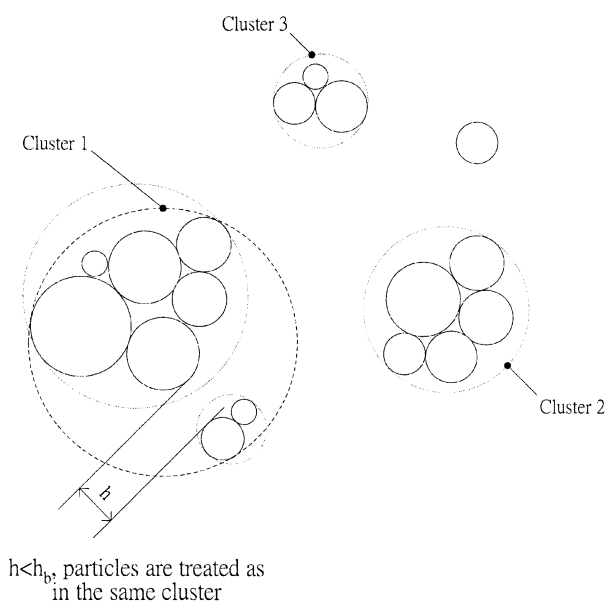


Figure 3: The formation of clusters.

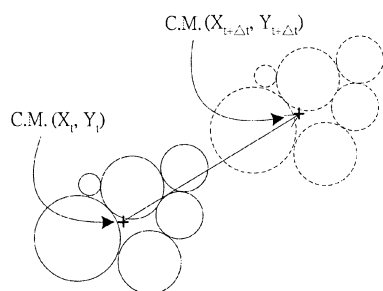


Figure 4: Center of mass of a cluster is the base point for Brownian motion.

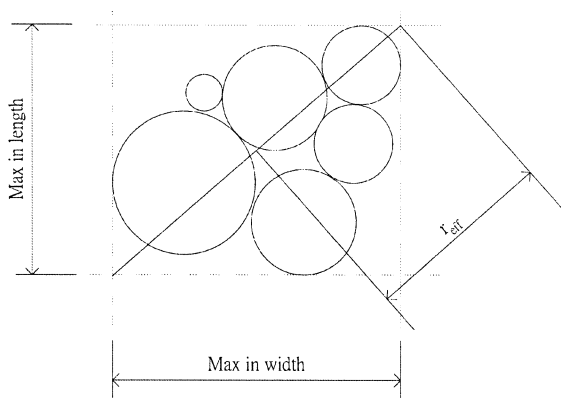


Figure 5: The effective radius of a cluster.

3.2 Geometrical contradiction check

It is not impossible to introduce geometrical contradiction between particles, because the displacement and direction of Brownian motion simulation of each cluster are randomly selected. The overlapping, which contradicts the physical phenomena, should be modified

accordingly. The strategy of considering the complexity of geometrical contradiction check is illustrated in Figure 6.

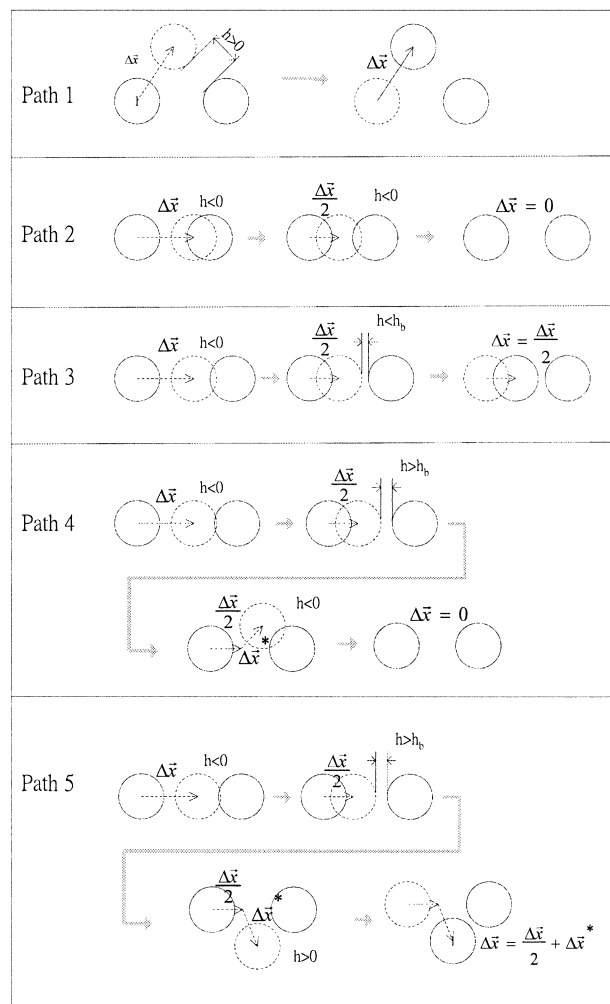


Figure 6: Different scenarios for contradiction check.

4 SIMULATION RESULTS

The agglomeration ratio of nanosized SiC particles in electro-plating solution is modeled. An electro-plating experiment was previously conducted to observe the adsorption of SiC particles on Ni [5]. Divalent cations Ni^{2+} in the plating suspension may adsorb on a negative surface of SiC in a weak acidic solution, and reverse the particle polarity to positive. Some particles will form clusters during electrophoresis process to the cathode due to the causes of potential instability. In order to resolve the effects of surface potential, the DEM simulation was conducted. The material properties and simulation parameters are summarized in Table 1.

Simulations with and without Brownian dynamics are conducted. To quantify the simulation results, degree of agglomeration (DoA) ratio is introduced:

$$DoA = \frac{\text{The total area of agglomerated particles}}{\text{The total area of all particles}} \times 100\%$$

The simulation results are shown in Figures 7, 8, and 9. Significant effects with Brownian motion simulation are observed. Without Brownian motion effects, DoA decreases with the increasing zeta potential. However, for the cases with Brownian motion, DoA fluctuates around 25% to 30%, while various zeta potentials contribute little to the values of DoA.

To assert our findings, we further calculate the average translation kinetic energy of a particle in one dimension. From the properties given in Table 1, the kinetic energy is $1/2 kT = 2.2 \times 10^{-21} J$, which is much greater than the kinetic energy for charge effect ($1/2 mv^2 = 3.2 \times 10^{-32} J$, if the mean particle size is 62 nm). Thus, roughly speaking, the kinetic energy of a particle by Brownian motion is significantly larger than that of the DLVO particle interaction, which implies the Brownian dynamics dominates in this case.

Table 1: Computational Parameters

Properties of SiC particle		
density	3.2×10^3	kg/m ³
Hamaker const.	10.9×10^{-20}	kg/m ³
Young's modulus	4.0×10^{11}	Gpa
Poisson ratio	0.16	
zeta potential	0 – 50	mV
Properties of medium (water)		
density	1.0×10^3	kg/m ³
viscosity	1.0×10^{-3}	Pa.s
temperature	300	K
Debye length (κ)	1.0×10^8	m
dielectric const.	80.1	
valence	2	
Operation conditions		
particle conc.	5.3	vol %
particle size dist.	10 – 100	nm
cal. time step	1.0×10^{-10}	s

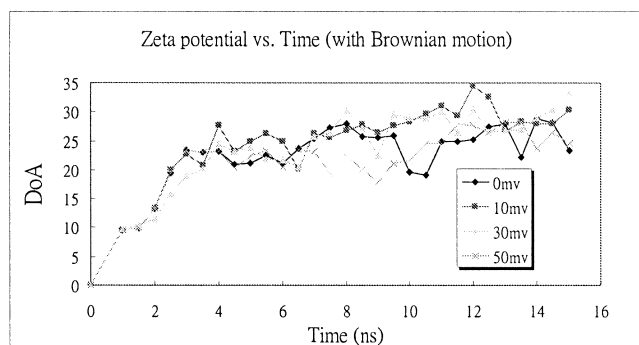


Figure 7: Zeta potential versus time with Brownian motion.

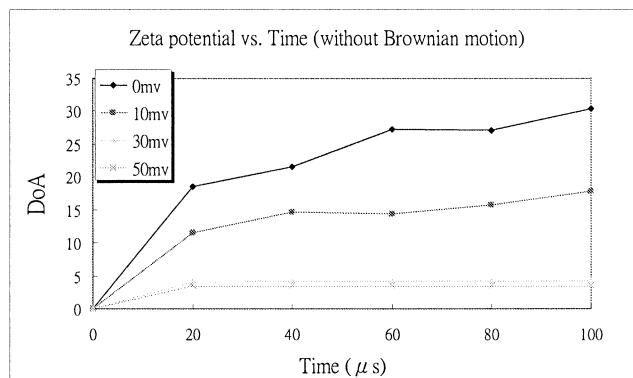


Figure 8: Zeta potential versus time without Brownian motion.

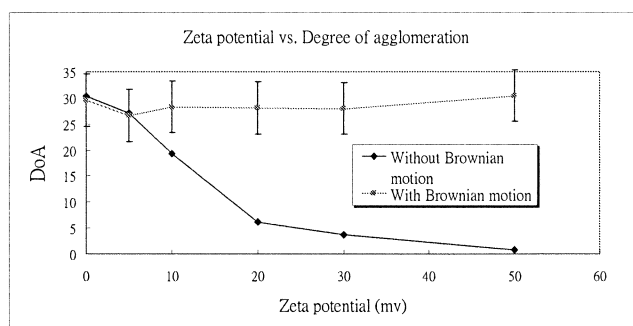


Figure 9: Zeta potential versus degree of agglomeration.

5 CONCLUSION

The dynamics process of agglomeration is clearly indicated by our simulation. From our preliminary results, we conclude that the Brownian dynamics dominates particle movement in dilute solution.

In this study, we have developed an integrated simulation toolbox that combines DEM with Brownian motion. Further simulations and experiments should be conducted to gain more fundamental understanding of particle agglomeration in dilute solution.

6 REFERENCES

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