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Size-concentration Dependent Analysis of Nanoparticle Agglomeration in Aqueous Suspension

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Abstract

A direct simulation Monte Carlo (DSMC) model is applied for the analysis of TiO_2 nanoparticles (TNP) agglomeration at various initial mass concentrations in an aqueous suspension. In this approach, TNP is simulated in a box. The agglomeration probability of NP is simulated within the context of Brownian motion. At diluted concentrations, model prediction is in quantitative agreement with the particle size distribution via dynamic light scattering measurement. This study shows that the applied DSMC model has the potential to predict the TNP size distribution in aqueous environment at the short time scale.

Keywords: DSMC, nanoparticles, agglomeration, Monte-Carlo, size-distribution

1. Introduction

TiO_2 nanoparticles (TNP) are widely utilized in applications such as self-cleaning materials, paints, cosmetics, medicine, etc. [1-4]. When TNP are in aqueous suspension, their sizes increase [5, 6]. As the size changes, the surface area to volume ratio of TNP alter, affecting their contact property. Therefore, TNP sizes have to be controlled. For example, to see the effects of TNP on living cells, the TNP sizes have to be fixed [7]. In coated work, the TNP diameters have to be maintained for the photocatalytic efficiency [8]. Recently, it was experimentally and theoretically shownthat the sizes of TNP which were immersed in solution, depended on many factors i.e., gravitational settling, pH, ionic strength, zeta potential, temperature of the solution, and hydration repulsion [9, 10]. However, TNP concentration, a factor dramatically affecting the sizes [5, 6] was not yet theoretically studied.

A modified Monte Carlo method called direct Monte Carlo simulation (DSMC) method was employed to theoretically describe the agglomeration diameters of particles [9-11]. DSMC is based on the choosing collision partners by a stochastic game, when the collision rates are known [12]. In the present study, DSMC is performed to calculate the agglomeration diameters in the context of Brownian motion with various concentrations of TNP from 15 mg/L to 35 mg/L. The system of TNP particles in the suspension state and just after suspension state are simulated which differs from the previous studies that studied the system of agglomeration at the long time scale in order of hour [9]. These simulated agglomeration diameters are compared with those from experiment by Dynamics Light Scattering (DLS) technique. The consistent result of the diameters

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at the diluted concentration, suggests that the applied DSMC with the related theories is a potential tool to predict the agglomeration of TNP at various concentration in aqueous suspension at the short time scale.

2. Materials and Methods

2.1 Experimental section of TNP agglomerate size evaluation.

The agglomerate sizes of TNP were quantified in an aqueous suspension, the Luria Broth (LB) medium which contained 0.17MNaCl, supplemented with 50 mg/L ampicillin, 0.25% glucose, and 0.25% IPTG (Isopropyl β-D-1-thiogalactopyranoside). The original powder form of P25 type, TNP was obtained from Evonik Digussa GmbH (Frankfurt, Germany), with the 21 nm primary size. In order to measure TNP agglomerate size, these particles were suspended in LB medium to obtain the TNP concentrations ranging from 15 mg/L to 35mg/L with the following procedure.

First, the powder was aliquoted into 15±5 μ kg in 1.5 mL micro centrifuge tube, sterilized for 15 minutes at 121°C, and dried at 100°C for 2 hours. Second, after the medium was filtered through a 0.2-μm filter to remove contaminants, the medium was added into the aliquot of the powder to obtain 5 mg/L suspension. The suspension was mixed for 10 seconds using a vortex mixer. Finally, the mixed suspension was serially diluted to achieve the concentrations. Immediately, the hydrodynamic diameters of the suspension particles were measured using DLS technique on a Zetasizer NanoZS (Malvern Instruments, UK) at room temperature. The size was reported as the distribution of particle number.

2.2 Simulation Algorithm

The constant number DSMC model of particles in a box was applied to describe TNP agglomeration diameters in the suspension. The simulation algorithm was described in Figure 1. The simulation was initialized with a random TNP distribution of N particles in a simulation box of volume V. The mass concentrations C, ranging from 15 – 35 mg/L were related to the volume by

$$V = \frac{\rho}{C}\sum_{i=1}^{N}\frac{4}{3}\pi r_i^3, \quad (1)$$

where ρ [kg/m^3] was the TNP density and r_i was the primary radius of TNP. Here, we employed N, the density, and the radius of 800 particles, 3900 kg/m^{3}and 21 nm, respectively.

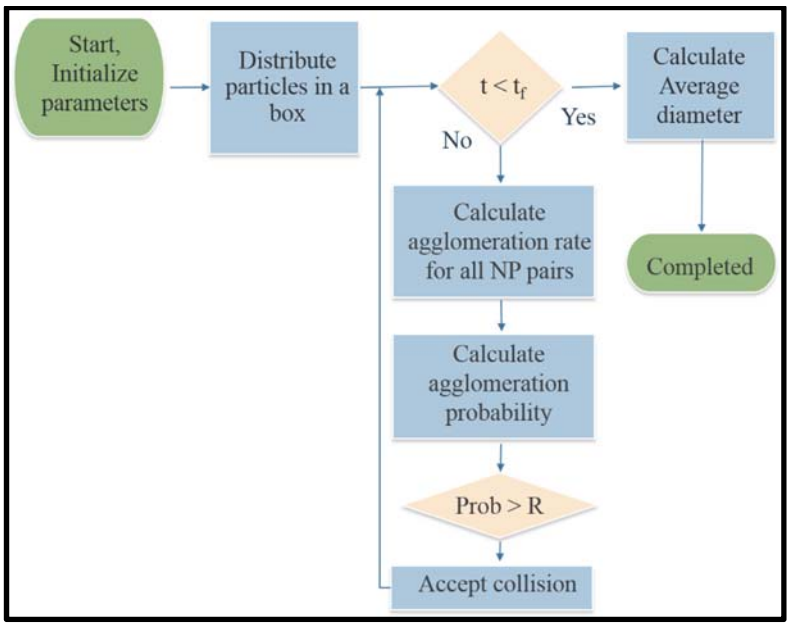

Figure 1. The flow chart diagram of the Monte Carlo particles simulation in a box.

When the time was less than final time, the particles were randomly moved in the box with periodic boundary condition. The system of TNP agglomeration in the box considered here was usually described by the Smoluchowski equation [11, 13]:

$$\frac{\partial n_k}{\partial t} = \frac{1}{2}\sum_{i=1}^{k-1} \beta_{i,k-i} n_i n_{k-i} - n_k \sum_{i=1}^{\infty} \beta_{i,k} n_i \,, \tag{2}$$

where t was time, n_k was the number concentration of the k-fraction, and $\beta_{i,k}$ is the collision rate or collision frequency of the particle pair (i, k). In DSMC method, this collision frequency of a particle pair was transformed to the collision probability of the particle pairs $P(i, k)$ following the equation:

$$P(i,k) = \frac{\beta^V_{i,k}}{\sum_{k=1}^{N}\sum_{i=1}^{N} \beta^V_{i,k}} \tag{3}$$

This particle pair was selected as a collision pair if the pair probability was greater than a random number generator R, whose values were uniformly distributed between 0 and 1. After the succeeding collisions, the size and position of the agglomerate pairs were calculated. These collision kinetics and calculations held until the system reached the final time which was 1.2×10^{-8} s, where time interval between collisions was set to be 10^{-10} s.

3. Results and Discussion

The work presented here was the average outcome of 800 particles over 10 simulations. As the accuracy of DSMC method may be varied with the number of particles, our first task was to carry out the relationship between average diameters with the varied particle numbers. From the simulations at the mass concentration of 15 mg/L, we found that the diameters varied with the number between 100-1,000 particles as shown in Figure 2. As indicated by the standard deviations, the diameters varied almost 10 nm when the number of particles was 100. When the numbers were close to 1,000, the diameter varied within 2 nm. This variation of the diameters with the particle numbers was in agreement with the results from another [9]. The decreased standard deviation with the increasing particle numbers was attributed to the increment of collision probability with the particle numbers. From this result, as the standard deviations of the average diameter simulated from 800 particles were less than 3% of the average diameter, this particle number was selected for the diameter determination at the other mass concentrations.

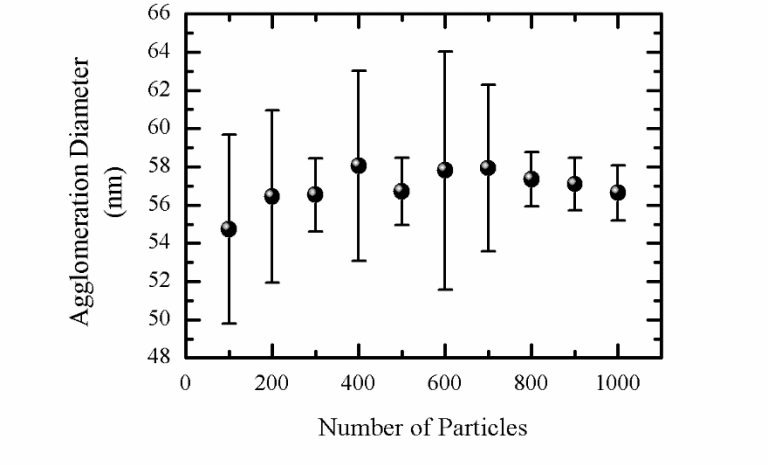

Figure 2. The accuracy of the agglomeration diameter depends on number of particles.

This result is based on the mass concentration of 15 mg/L and the replicated 10 simulations. The diameter standard deviations are indicated by bars (Figure 2). We continued evaluating the average diameters of TNP agglomeration using DSMC method at the other TNP mass concentrations which were 20, 25, 30, and 35 mg/L. The error bar was high at the mass concentration of more than 20 mg/L, indicating the variation of factors affecting agglomeration at these concentrations. The results from the error bar indicated the standard error averaged from 10 repeated measurements. DSMC were compared to those from experiment as shown in Figure 3. From the experiment on TNP in the present study by DLS technique, when the TNP concentrations were increased from 15 mg/L to 35 mg/L, the average diameters were increased. The error bar indicated the standard error averaged from three repeated measurements. The error bar span was wide in the range of concentration greater than 20 mg/L, suggesting some factors affect the diameter e.g. pH of the dispersion solution [14]. Similar behavior of the other type of nanoparticles was also observed. Iron oxide nanoparticle agglomeration diameter was altered with the increased concentration, with a higher concentration than that of TNP [14]. As shown in the figure, with the concentration between 10 - 50 mg/L, the iron oxide agglomeration diameter was not changed. Iron oxide agglomeration diameter was likely to change at the concentration of

greater than 100 mg/L (data not shown in the figure), whereas, TNP or TiO_2 nanoparticle agglomeration diameter was likely to change at the concentration greater than 20 mg/L. These experimental findings of both nanoparticle types were consistent with the result predicted from DSMC simulation. The average diameters were increased with the mass concentrations. The average diameters of 15 mg/L and 20 mg/L were consistent with those from the experiment. This indicated that Brownian motion of TNP in suspension is dominated at a range of TNP concentration. i.e., at the concentrations of 15 mg/L and 20 mg/L.

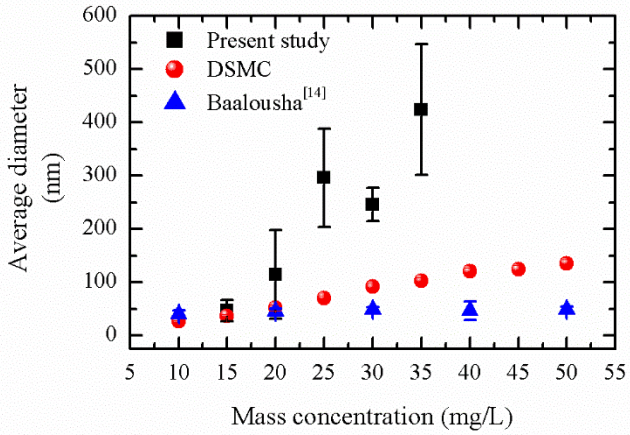

Figure 3. There are average agglomeration diameters as a function of TNP particle numbers.

The TNP diameter data from DLS in the present study is denoted by rectangular symbols. The vertical bars represent standard error from three replications. Iron oxide diameter data from Baalousha [14] is shown in triangular symbols. The data from DSMC method is denoted by circular symbols. The vertical bars (which are very small) represent standard deviation based on 10 replicated simulations.

At the concentration of TNP higher than 20 mg/L, the results from DSMC were not in agreement with those from DLS experiment. Actually, in the system, there were factors depended on particle concentrations that affected the agglomeration diameters such as gravitational settling, pH, ionic strength, zeta potential, and the temperature of the solution [9]. These factors possibly significantly affected the diameters at the high concentrations, but not the diluted concentrations. Therefore, to accurately predict diameters, gravitational force due to Stoke's sedimentation [9, 15] and the interaction between particles as described by the well-known DLVO theory should be considered combining with the DSMC method [6, 7, 10, 16, 17].

In the experiment, the mechanism of nanoparticle agglomeration just after suspension state was still unclear [7]. Whereas in the present study, particle agglomeration during suspension and just after suspension state was simulated by DSMC. At the beginning of dispersion, particles were randomly moved with different random velocities in three dimensional directions. After that, during a time step, they were allowed to collide and had the succeeding collision if the collision probability was greater than a random number. In the succeeding collision, the distance between a collision pair was set to be not greater than the primary diameter. In the next time step, the agglomeration of the pair could be altered according to the random velocity of the particles. Finally, the agglomeration diameter of the final configuration was calculated at the final time. The agreement of agglomeration diameter performed by DSMC with the experiment results at the diluted concentration suggested the possible mechanism explaining the system just after suspension state. However, this mechanism failed to explain the situation at the higher concentrations.

4. Conclusions

In summary, the DSMC method describing TNP agglomeration diameters at the short time scale was applied at various concentrations of TNP. This applied DSMC reasonably predicted the diameters at the diluted concentrations. TNP are considered as model nanoparticles. Thus, DSMC could be a potential tool to predict the agglomeration diameters of nanoparticles at various concentrations in aqueous suspension. The extension of this method by combination of gravitational settling and DLVO theory into DSMC method to predict the diameters at the high concentrations, would provide a wide utilization insight to users who interested in TNP and nanoparticle agglomeration in aqueous suspension at the short time scale.

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