

Modeling Aggregation and Size Distribution of Nanoparticles with Monte Carlo Simulation

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ABSTRACT

The size distribution of the nanoparticles and their aggregates is crucial for predictions of the fate and transport of nanoparticles in the environment. A computational model was developed, based on a Monte Carlo simulation, to predict the aggregation rate and size distribution of nanoparticles under various simulated environmental conditions. Model performance compared favorably with DLS data demonstrating the potential of the present modeling approach for use in environmental analysis of the transport and fate of nanoparticles.

Keyword: *nanoparticle, aggregation, size distribution, sedimentation, Monte Carlo simulation*

1 INTRODUCTION

Rapid technological advances in nanotechnology have raised public concern regarding the potential environmental releases and toxicity of engineered nanoparticles [1-4]. The environmental impact of engineered nanoparticles (eNMs) is governed by the receptor's exposure to these particles and thus their concentration in the environmental media of exposure. Of particular interest is the impact of eNMs in the aquatic environment. The transport and fate of eNMs in aqueous systems, as is the case with all particle-bound chemicals [5, 6], is affected by the particle size and hence the aggregation state of such particles. For example, it is known that nanoparticles tend to aggregate in aqueous systems [7-10] with the aggregation tendency being a function of environmental conditions such as pH, ionic strength and temperature.

Detailed and complete experimental mapping of the nanoparticle size distributions over the entire range of environmental water chemistry and nanoparticle properties is impractical. Therefore, predictive models that are verified with experimental data could be particularly useful in environmental impact assessment models to determine the aggregation tendency of nanoparticles and the resulting particle size distribution (PSD). Accordingly, the present work focused on the development of a computational

model, based on a constant-number kinetic Monte Carlo [11] simulation approach, to predict the aggregation rate and size distribution of nanoparticles under various simulated environmental conditions.

2 METHOD

The modeling approach followed the "particles in a box" simulation approach with allowance for particle sedimentation. The likelihood of nanoparticle aggregation was determined, based on the classical DLVO theory [7, 12, 13]. The classical DLVO theory states that the total interaction energy is the sum of van der Waals attraction energy and the electric double layer repulsion energy [8, 12-14]. The electric double layer repulsion energy takes two forms, depending on the relative thickness of the double layer with respect to the size of the nanoparticles [7, 12-15] [1]. The van der Waals attraction energy [7, 8, 12-15] is a function of the ionic strength of the solution.

In the simulation approach a cubical box is constructed with dimension that allows N primary nanoparticles to occupy the box at a prescribed concentration. The primary nanoparticles are randomly introduced into the box while avoiding overlap. The particle number density is adjusted when aggregation occurs to ensure mass conservation in the box. The likelihood of aggregation of particle pair is determined from the aggregation kernel [11-15] whereby both the DLVO theory and the Brownian aggregation kernel [11, 13, 15, 16] are considered.

Comparison of the average nanoparticle size with DLS measurements require considerations of the extent of sedimentation that may occur during the DLS measurement. For example, DLS measurements to assess nanoparticle stability are often carried out over time periods of several hours. The particle sedimentation Stokes' terminal sedimentation velocity is proportional to r^2 , where r is the particle radius [17]; therefore, the sedimentation distance, l , during a time step dt is given as $l \propto r^2 dt$. The distance traveled due to Brownian motion, $\langle x \rangle$, over the same time

interval is given as $\langle x \rangle = (2 \cdot D \cdot dt)^{1/2}$, where D is the Brownian diffusivity. Particle movement in the simulation box considers the movement of particles due to both sedimentation and Brownian motion.

When a pair of nanoparticles are determined to aggregate, the time step for this event is calculated following the approach of Smith et al [11]. When a nanoparticle aggregates with another nanoparticle or an existing aggregate, or when they are removed from the simulation box due to sedimentation, the number of nanoparticles in the box is reduced and thus new particles are added in order to conserve the total number of particles (primary and secondary). The size of the replacement particle is selected from a portion of particle size distribution, estimated from the particle size distribution of the simulation box. However, in order to ensure mass conservation, the size of the box is expanded to keep the mass concentration in the box constant.

Following the above approach, the PSD is followed over time computing the mean nanoparticle size as it develops. Comparison of model results with experimental data was carried out by accounting for the impact of particle sedimentation on size distribution measurements via dynamic light scattering (DLS).

3. DISCUSSION

The rate of nanoparticles aggregation depends on the size of nanoparticles, ionic strength of the medium, zeta potential (ζ) of the suspension, and the Hamaker constant of the suspension [18]. Ions in the solution suppress the electric double layer and thus reduce the repulsion energy between particles. Therefore nanoparticles in a solution with higher ionic strength are more likely to aggregate. ζ -potential increases with increasing difference between the pH of the suspension and the isoelectric point (IEP) of the nanoparticle. IEP is the suspension pH where there is no net charge at the surface of the nanoparticle, and thus the electric double layer vanishes and the ζ -potential is identically zero. As pH deviates away from the IEP, the surface charge begins to build up, as do the thickness of the double layer and the magnitude of ζ -potential. As ζ -potential increases, the repulsion energy also increases, resulting in a more stable suspension with nanoparticles with diminished aggregation tendency. The van der Waals attraction energy increases with the Hamaker. Therefore, as the Hamaker constant increases the attraction energy increases and the tendency for nanoparticle aggregation increases.

An illustration of the simulation results is provided in Fig.1 showing the effect of ionic strength on the computed average particle size for TiO₂ nanoparticles of primary size of 21 nm. As the ionic strength increases the tendency of

the nanoparticles to aggregate also increases resulting in larger size aggregates.

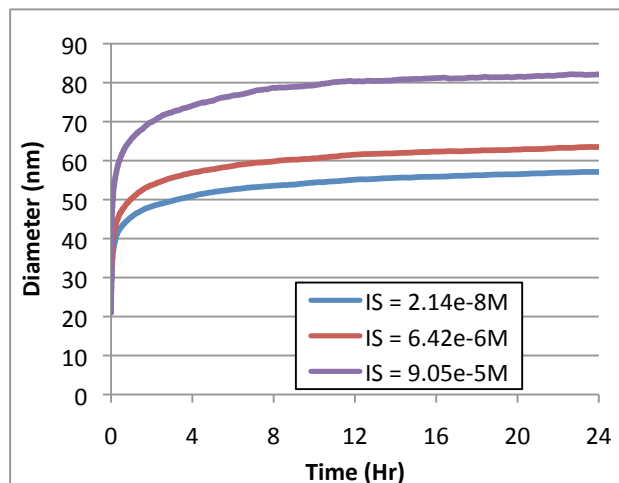


Figure 1 Evolution of nanoparticle size at various ionic strength values

Similarly, as the solution pH rises above or below the isoelectric point (IEP), particles aggregation increases (Fig 2).

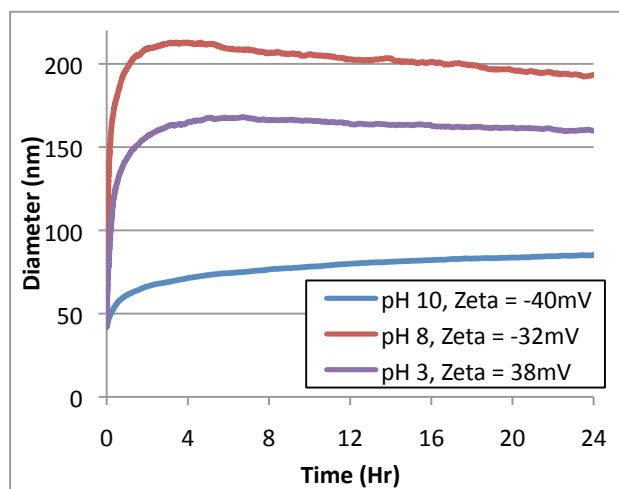


Figure 2 Evolution of nanoparticle sizes at various pH values

Comparison of the model simulation results with experimental DLS data is provided in the example of Fig. 3 for TiO₂ nanoparticles of 21 nm primary size at pH of 3 and ionic strength of 4.257×10^{-6} M. These results show that the mean nanoparticle size rapidly increase before reaching a relative stable size. The initial rapid increase is the result of the first wave of nanoparticle aggregation. Although these large particles are under the influence of sedimentation, it takes some time for the particles to reach the bottom of the simulation box as would be the case within the volume of the DLS laser beam. Therefore a delay is observed in the evolution of particle sizes before the mean particle size stabilizes. Nonetheless, the simulation

results are in remarkable agreement with the experimental data considering the variability in the measurements in a system in which aggregation and sedimentation occur simultaneously.

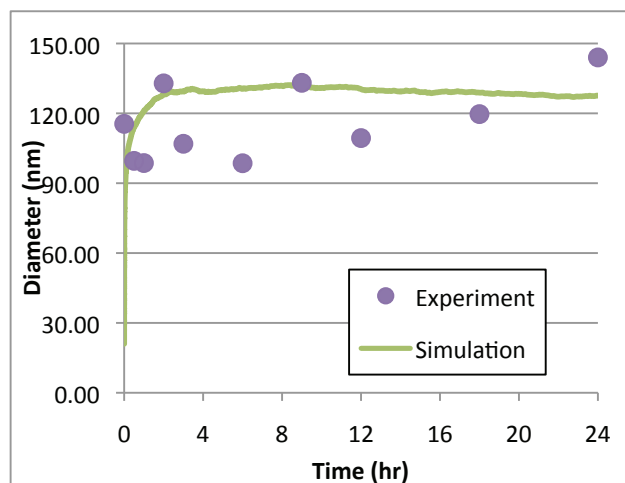


Figure 3. Evolution of particle sizes at pH = 3

4 CONCLUSION

A model based on constant number dynamic Monte Carlo method was developed to describe nanoparticle aggregation behavior in aquatic suspensions. Model simulations confirmed importance of accounting for sedimentation when comparing the results with DLS measurements. The present results are encouraging and the modeling approach is being expanded to incorporate other factors that may impact the evolution of the size distribution of nanoparticles such as disaggregation and steric effects.

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