Simulation of Cluster Formation from Kaolinite Suspensions

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Abstract

The behavior of kaolinite suspensions has been studied by Brownian dynamics simulation, considering the action of DLVO forces, and the results are reported in this paper. A coarse grained model for kaolinite particles was built to facilitate the computation. Cluster formation from kaolinite suspensions was found at low pH (pH 5); in contrast, kaolinite particles were well dispersed at high pH (pH 8). This distinguishing feature is mainly due to the anisotropic surface properties of kaolinite particles and their pH dependence. At pH 5, the particles are aggregated by attraction between the negative silica face surface and the positive alumina face surface, as well as by the interaction between the negative edge surface and the positive alumina face surface. However, at pH 8, all the surfaces are negatively charged, resulting in a well dispersed kaolinite suspension. The simulated results were successfully validated by SEM imaging with WETSEM capsules. Cluster formation at low pH is believed to explain success in the reverse flotation of kaolinite from bauxite ore at pH 4-5 with a primary amine collector.

Keywords

Brownian dynamics simulation, Kaolinite suspension, Cluster formation, pH effect

1. Introduction

The behavior of kaolinite suspensions is of significant importance in many areas of technology, including mineral processing, specifically flotation and dewatering processes. Understanding the surface chemistry of kaolinite particle interactions is fundamental for control of suspension stability and rheological behavior. Due to the unique features of kaolinite particles, including their anisotropic surface charge and platy particle shape, the characteristics of kaolinite particle interactions can be very complex.

Generally, the structure of clusters arising from particle interactions is considered to be a manifestation of the interplay of the electrostatic force and the van der Waals force (Van Olphen 1977; Mitchell and Soga 1976; Palomino and Santamarina 2005). The primary kaolinite particles are anisotropic with two face surfaces and one edge surface as is expected from the kaolinite structure shown in Figure 1. H. van Olphen described several modes of particle interaction: face to face, face to edge, and edge to edge (Van Olphen 1977). One of the three modes of particle interactions can be dominant, yet a mixture of two or three modes may exist. It is expected that a three dimensional card-house structure will be formed with edge-face and edge-edge interactions. O'Brien suggested a face to face mode of interaction accounted for the aggregated structure as well, resulting in a large void ratio for the structure as shown in Figure 2 (O'Brien 1971).

Figure 1. Crystal structure of kaolinite. Red: Oxygen; Yellow: Silicon; Purple: Aluminum; White: Hydrogen.

Due to the misunderstanding of the surface properties of kaolinite particles, the significance of face to edge electrostatic interaction has been over-estimated. Past researchers have incorrectly considered that the two kaolinite face surfaces are negatively charged and that the edge surface is positively charged. Recent results show that the alumina face surface and the silica face surface carry opposite charges at low pH, and the edge surface is negatively charged above pH 4 (Gupta and Miller 2010; Liu et al. 2014). The face to face electrostatic attraction is as important as, and even more important than, the face to edge electrostatic interaction. In other cases, for example at high ionic strength, the electric double layer is compressed, and the van der Waals interaction is dominant. In this regard, the interactions of face to face, face to edge and edge to edge are all possible due to the van der Waals attraction.

Figure 2. Stairstep card-house fabric of aggregated kaolinite particles (O'Brien 1971).

The fabric of clusters which form in kaolinite suspensions has been anticipated based on the measurement of sedimentation and viscosity as a function of pH and ionic strength. The van der Waals attraction is expected to prevail beyond a critical pH level and a threshold ionic concentration (Palomino and Santamarina 2005; Rand and Melton 1977). Cluster structure has been inferred from the hypothesis that the face to edge interaction causes higher apparent viscosity and larger sedimentation volume, while the face to face interaction results in lower apparent viscosity and smaller sedimentation volume for the kaolinite suspension (Schofield and Samson 1954; Palomino and Santamarina 2005). At low pH (~pH 3), a face to face interaction is expected; at intermediate pH (pH 7-9) and intermediate salt concentrations (3mM to 100mM),

suspension settling behavior suggests a mixture of particle interactions, from an initially dispersed suspension, eventually having edge to face interaction (Palomino and Santamarina 2005).

Direct examination of kaolinite clusters in-situ is difficult because the primary particles are below one micron in size and complex cluster structures are formed in the aqueous suspension. Imaging in a wet environment with such small particle sizes is a challenge for modern instruments. Some researchers have tried direct SEM imaging of kaolinite clusters by a freeze-drying technique, or cryo-SEM (Zbik et al. 2008; Pierre et al. 1995; Gupta et al. 2011; O'Brien 1971). Complex structures of particle clusters have been presented as a function of pH. However, concern exists if the cluster structure is maintained during drying or freezing. Further, the resolution of SEM without high vacuum is limited and discrimination of the two face surfaces of kaolinite is not achieved.

Simulation is another possible approach to describe the structure of kaolinite clusters. Recently particle interactions using a meso-scale simulation technique have been reported (Markutsya et al. 2008; Suter et al. 2009; Odriozola et al. 2004; Anderson et al. 2005). Molecular dynamics (MD) simulations on a mesoscopic scale have been carried out to study the dispersion of disc shaped Laponite clay platelets (Kutter et al. 2000). Markutsya et al. (2008) demonstrated that the computational efficiency for the simulation of nanoparticle aggregation using Brownian dynamics (BD) is much greater than using MD, due to additional calculations for the aggregates and the solvent in MD simulations. Unfortunately, only spherical particles or platy particles with one face surface have been simulated. Kaolinite cluster formation with the complex surface chemistry of kaolinite particles has not been studied. In this regard, a Brownian dynamics simulation of

kaolinite particle interactions has been accomplished for the first time, with each kaolinite particle having two different basal plane surfaces (two different face surfaces) and an edge surface. The results are reported in this contribution.

2. Experimental Methods

2.1 Coarse Grained Model

A coarse grained model of kaolinite particles has been constructed to include the surface properties of the kaolinite particles and to facilitate computations. Two types of spheres were used to construct the alumina and the silica face surfaces of a hexagonal platy shaped particle as shown in Figure 3. Each sphere had a diameter of 1 Å to facilitate computation. One alumina sphere and one silica sphere with a vertical distance (z direction in Figure 3B) of 1 Å from their centers were grouped as one kaolinite unit. The distance between the centers of two adjacent units was 2 Å. A typical kaolinite particle contained 61 units and 122 spheres in total, as shown in Figure 3. The surface charge of each sphere was assigned based on experimental AFM data (Gupta and Miller 2010; Liu et al. 2014). Appropriate coding was accomplished in Moltemplate 1.17 to generate the coordination of coarse grained particles (Jewett et al. 2013).

Figure 3. Coarse grained model for kaolinite particles (A) Top view (B) Side view. Cyan spheres represent the alumina face surface of the kaolinite particle, and pink spheres represent the silica face surface of the kaolinite particle.

2.2 Simulation Details

LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) was used for the simulation of kaolinite particle interactions (Plimpton et al. 2007). Each kaolinite particle was built using the coarse grained model introduced in Section 2.1. All the simulations were performed in a cubic cell of (250 Å × 250 Å × 250 Å) in size, using

periodic boundary conditions in all three dimensions. The number of particles was added according to the desired particle concentration for the kaolinite suspension.

The solvent (water) was treated as a structureless dielectric continuum characterized by its relative permittivity, ϵ_r , which was 78 in this case. Monovalent salt and counterions were represented implicitly by the Debye length, κ^{-1} . For the 1 mM KCl solution used in this study, the Debye length was calculated to be 9.8 Å.

The interactions between colloidal particles were computed by the DLVO model (Derjaguin-Landau-Vervey-Overbeek), which describes the balance between the van der Waals potential and electrostatic potential.

Due to the existence of electrolytes, the electrostatic potential is expressed in the form of screened Coulomb or Yukawa potential, as described by the following equation.

$$U_{Yukawa} = A \frac{e^{-\kappa r}}{r} \quad r < r_c \quad (1)$$

$$A = 2 \times \pi \times a \times \epsilon_0 \times \epsilon_r \times \kappa \times \psi^2 \quad (2)$$

Where r_c is the cutoff, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the fluid medium, κ is the inverse screening length, and ψ is the surface potential.

The van der Waals potential between two colloidal particles (spheres) is expressed by the following equation (Hamaker 1937; Everaers and Ejtehadi 2003):

$$U_{vdw} = -\frac{A_{12}}{6} \left[\frac{2a_1a_2}{r_{12}^2 - (a_1 + a_2)^2} + \frac{2a_1a_2}{r_{12}^2 - (a_1 - a_2)^2} + \ln \left(\frac{r_{12}^2 - (a_1 + a_2)^2}{r_{12}^2 - (a_1 - a_2)^2} \right) \right] \quad (3)$$

A_{12} refers to Hamaker's constant ($A_{\text{Silica-Silica}}=6.5 \times 10^{-20} \text{J}$, $A_{\text{Silica-Alumina}}=9.94 \times 10^{-20} \text{J}$, $A_{\text{Alumina-Alumina}}=1.52 \times 10^{-19} \text{J}$) (Butt et al. 2006, Gupta and Miller 2010), a_1 and a_2 are the

radii of the two colloidal particles (spheres), r_{12} is the distance between two colloidal particles (spheres).

Therefore, the total DLVO potential is expressed as follows.

$$U_{DLVO} = U_{yukawa} + U_{vdw} \quad (4)$$

In fact the results for the potential between two primary particles (hexagon plates) was a summation of the colloidal potential, considering all colloids (spheres) that were made up of each primary particle (hexagon plates). It was obvious that the potential calculation between spheres in the same particle was not necessary and was excluded.

In addition, in order to avoid particle penetration during collision, a shifted and truncated Lennard-Jones potential was used for a distance $r_{12} \leq 2^{1/6}$.

$$U_{lj} = 4\epsilon_{lj} \left(\left(\frac{\sigma_{lj}}{r_{12}} \right)^{12} - \left(\frac{\sigma_{lj}}{r_{12}} \right)^6 \right) + \epsilon_{lj} \quad r_{12} \leq 2^{1/6} \quad (5)$$

Where ϵ_{lj} and σ_{lj} are the Lennard-Jones parameters, with $\epsilon_{lj}=0.5k_B T$ and $\sigma_{lj}=1\text{\AA}$ in all simulations.

The surface charge density used in the simulation was assigned as shown in Table 1. The simulation study was designed to provide a qualitative analysis for the formation of cluster structure as a function of pH, simulation time and ionic strength, etc., and in this case, the assigned surface charge of kaolinite particles was suitable for our research purpose (Delhorme et al. 2012; Odriozola et al. 2004). As described in the literature and applied in the simulations, the silica surface of a kaolinite particle is negatively charged and the alumina surface of a kaolinite particle is positively charged at low pH (pH 5). Both surfaces are negatively charged at high pH (pH 8) (Gupta and Miller 2010). In the simulations, the charge of the edge surface of a kaolinite particle was the average of the

charges of the two basal plane surfaces, which is negative at both pH 5 and pH 8 but more negative at pH 8 (Liu et al. 2014).

Table 1. The surface charge density of silica and alumina surfaces at 1mM KCl used in the simulation.

A random initial configuration with kaolinite particles was established first. Brownian dynamics was applied for the simulation of kaolinite particle interactions. A Langevin thermostat was applied to model the interaction of particles with a background implicit solvent (Schneider and Stoll 1978). Constant NVE (constant volume and constant energy) integration was performed to update the position and velocity of the particles at each timestep. The temperature of the system was set to be 298K. For the first 500 ps of the simulation, a timestep of 1 fs was used. Later, timesteps of 2 fs were used for a total simulation of 10 ns, 20 ns, or 30 ns.

2.3 Cluster Identification and Description

The following terms used in this paper need to be clarified before further discussion.

1) Particle Structure

The particle structure established by the aggregation of kaolinite particles is discussed in terms of interactions of surfaces, and the size distribution of structures. It is expressed as number of particles per structure, and the relative exposure of surfaces (alumina and silica faces).

2) Particle Cluster

A cluster consists of a particle structure and associated water. In this regard the

cluster size/shape and associated water is defined by the ellipsoid which envelopes the particle structure.

3) Cluster Size, Shape, and Composition

Cluster size is described from ellipsoid dimensions and number of particles per cluster. Cluster shape is described by the aspect ratio and its variation. Finally, then, the cluster composition is described by the water content.

The center of mass (C.M.) of each particle in the system was computed during the simulation, which is an available output option in LAMMPS. When the simulation finished, the aggregated particle structure size, defined as the number of particles in a specific particle structure, was determined with an implemented package ‘nnclust’ in R software by finding the nearest neighbors of each particle. The maximum separation distance of the C.M. for two adjacent particles, was selected as 16 Å, the criterion for determining if the particles are in the same aggregated particle structure. The distance between each pair of particles was calculated and in this way, based on this distance criterion, aggregated particle structure identity was established.

2.4 Surface Area of Particle Structures

The external surface area of the particles in each aggregated particle structure was calculated by the EDTsurf method using the technique of Euclidean Distance Transform (EDT) (Xu and Zhang 2009). Triangulated mesh surfaces were constructed from volumetric solids by a Vertex-Connected Marching Cube algorithm (Lorensen and Cline 1987; Xu and Zhang 2009). Distance Transform is a transformation that converts a digital binary image to another grey scale image, where the value of each pixel in the image is the minimum distance from the background to the pixel by a predefined distance function.

The distance function for Euclidean distance between two points (x_1, y_1, z_1) and (x_2, y_2, z_2) is described by the following equation:

$$d_{Euclidean} = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2} \quad (6)$$

In this way, the boundary points or the surface of an object O are determined by calculating the distance between a random point x and point y from the object O . Using the space-filling method, the object is filled by volumetric solids (Greer and Bush 1978; Juffer and Vogel 1998). The voxels whose Euclidean distances were less than the probe radius (1.4 Å) were removed. The remaining solid was the surface of the object. The Vertex-Connected Marching Cube method was applied to construct the triangulated surfaces from the volumetric models. By way of example, analysis of the particle structure surface for a cluster is considered in sections 3.1 and 3.2.

After being constructed with the EDTsurf method, the aggregated particle structures were exported to individual files for analysis of the surface area. The surface areas of silica faces and alumina faces in an aggregated particle structure were estimated by MeshLab based on their color (Cignoni et al. 2008).

2.5 SEM Imaging

A concentrated kaolinite suspension (~50% wt) was prepared at the desired pH for SEM imaging. A WETSEM capsule (QX-102, QuantomiX Ltd., Israel) allows the SEM imaging of a fully hydrated kaolinite suspension at high vacuum (Barshack et al. 2004). 15 µl of the suspension were injected into a well-sealed WETSEM capsule, which was separated from the interior of the electron microscope by a thin, electron-transparent partition membrane. This membrane was strong enough to sustain a 1 atm pressure difference and, in this way, the sample inside the capsule was maintained at atmospheric

pressure while the SEM chamber reached high vacuum. The electrons penetrated a few microns into the wet cluster and a SEM image of the cluster structure was obtained.

3. Results and Discussion

3.1 Effect of pH on Particle Interactions and Particle Structures

Figures 4 (A) and (B) show snapshots of 1000 kaolinite particles at pH 5 and pH 8 after 10 ns simulation time. A size distribution of the particles was used in the simulations. The particle size was described by the number of spheres on the side of a hexagon layer, The ratio of the number of particles with a size of 7, 6, 5, 4, 3 spheres was 1:2:4:2:1. The number of particles with their corresponding particle size is presented in Table 2. At pH 5, the silica face surfaces and the edge surfaces of kaolinite were negatively charged; the alumina face surfaces were positively charged. The particles were stacked layer by layer with the silica face surface attracted to the alumina face surface; after a certain thickness of stacking occurred, the edge surface started to be attracted to the alumina face surface. In this way, more silica face surfaces were expected to be exposed to the environment when compared to the exposure of alumina face surfaces. The observed aggregated particle structure was close to that expected by O'Brien as shown in Figure 2 (O'Brien 1971). In contrast, at pH 8, all surfaces of the kaolinite particles were negatively charged. The particles were well dispersed, and no obvious interactions were observed at pH 8.

The surface area of the aggregated particle structure at pH 5 was calculated as $258,865 \text{ \AA}^2$ by the EDTsurf method, and the surface area of the dispersed particles at pH 8 was $804,950 \text{ \AA}^2$, which is almost 4 times larger than that calculated at pH 5. Moreover, the volume of the aggregated particle structure was $928,776 \text{ \AA}^3$ at pH 5 and the volume of

the dispersed particles at pH 8 was 1,628,250 Å³. Note the volume calculated from the software is always overestimated since the boundary of each aggregated structure or particle dispersed is overestimated by the analyzing probe. In any case, the results indicated that the particles had significant aggregation and the particle structures were compacted at pH 5, accounting for the smaller surface area and smaller volume; in contrast, the particles were well dispersed at pH 8, resulting in a larger surface area and larger volume.

Table 2. Number of particles and their corresponding particle size in the simulation.

Figure 4. (A) Brownian dynamics simulation snapshot of 1000 kaolinite particles at pH 5 after 10 ns simulation time; (B) snapshot of 1000 kaolinite particles at pH 8 after 10 ns simulation time. Pink spheres represent the silica face surfaces of kaolinite particles, and cyan spheres represent the alumina face surfaces of kaolinite particles.

Figure 5 (A) shows the center of mass (C.M.) for kaolinite particles and identification of aggregated particle structures at pH 5. Each dot represents the C.M. of one kaolinite particle. The particles belonging to one cluster are represented by one color. As mentioned before, many aggregated particle structures were formed at pH 5; however, at pH 8 most particles were well dispersed. See Figure 5 (B). The results indicated that at low pH, the alumina face to silica face interaction and the alumina face to edge surface interaction were dominant, mainly due to the electrostatic attraction. Note that the equilibrium state was not reached for pH 5; a more complicated aggregated particle structure may be expected with longer simulation times.

Figure 5. (A) Representation of the center of mass (C.M.) of kaolinite particles and aggregated particle structure identification (by color) at pH 5 after 10 ns simulation time (B) Representation of the C.M. of kaolinite particles and aggregated particle structure identification (by color) at pH 8 after 10 ns simulation time.

Typical aggregated particle structures from the simulation at pH 5 are shown individually in Figure 6, where the face to face interactions and face to edge interactions are observed. The total surface area of each aggregated particle structure and the surface area of the alumina face and the silica face were calculated and summarized in Table 3. Note that the edge surfaces of the kaolinite particles account for the surface area of the silica and alumina surfaces as well. The percent of the silica surface area or the alumina surface area over the total aggregated particle structure surface area was very close for individual aggregated particle structures and the average percent of the silica surface area and the alumina surface area for the 6 aggregated particle structures described in Table 3 were found to be 54.9% and 45.1% respectively. About a 10% higher surface area was found for the silica surface in the aggregated particle structure.

Figure 6. Representation of typical aggregated particle structures formed at pH 5 after 10 ns simulation time. The particle structures were filled with volumetric solids by the EDTsurf method. The pink surfaces represent the silica face surfaces of the kaolinite particles, and the cyan surfaces represent the alumina face surfaces of the kaolinite particles.

Table 3. Surface areas of typical aggregated particle structures after simulation of 10 ns, and areas of the silica and the alumina surfaces in each particle structure. The percent of each surface area (silica and alumina) for the particle structures is listed together with the average of the six particle structures. The particle structure number corresponds to that labeled in Figure 6.

3.2 Ellipsoid Enveloped Clusters

The composition of the kaolinite clusters with respect to water content should be considered in order to explain flotation phenomena, sedimentation, consolidation, and other mineral processing processes.

The water content in the cluster can be described using an ellipsoid model, in which an ellipsoid is fitted to envelope the aggregated particle structure. The same center

of mass of the aggregated particle structure was used for ellipsoid fitting the cluster structure. The bounding box of each cluster was computed and the volume of the ellipsoid model was calculated. The original particle structure volume and the ellipsoid volume of the clusters are summarized in Table 4 (for the simulation of 1000 particles with a simulation time of 10 ns). The volume percent of kaolinite particles for clusters in the ellipsoid model is presented, as well. With a more complex cluster structure, less percent solids occurred in the ellipsoid model. This indicated that more water was included in the clusters having a more complex structure. In contrast, the results also suggested that the percent of particles in the ellipsoid model increased significantly with smaller cluster size. In fact, previous studies have suggested that the porosity of the clusters increases with the growth of the clusters (Hogg 2013; Vold 1963; Klimpel and Hogg 1991). Note that the percent solids and the cluster size were not linearly related; this is due to the fact that the amount of water included in the ellipsoid model was influenced by the aspect ratio of the clusters. Of course a larger aspect ratio for a cluster will result in more water contained within the cluster for the ellipsoid model, although the cluster size and structure should be taken into consideration, as well. For big clusters (cluster number 1-31), a sudden increase of the aspect ratio of the clusters generally accounts for a decrease in the percent solids. However, for small clusters (cluster number 32-47), similar phenomena are not observed due to a small number of particles being fitted by the ellipsoid model. The average percent solids for the ellipsoid model cluster was 48.4%, which helps to describe the composition of kaolinite clusters.

Some parameters (porosity, density and relative particle area) which indicated the composition of kaolinite clusters, as measured by experimental methods and reported in

the literature, are summarized in Table 5. At low pH (4-6), the porosity of clusters is significantly larger than that of the clusters at high pH (8). The large porosity and low density suggest the existence of water in large amounts in the clusters. However, these experimental data are not suitable for quantitative comparison with the cluster simulation results because the experimental data are analyzed based on cryo-SEM images for which the original cluster structure is not preserved during the freezing process (Du et al. 2009).

Table 4. Volume of each cluster, volume for the cluster enveloped by an ellipsoid, and the cluster aspect ratio. The percent solids for each cluster was determined from the ellipsoid volume.

Table 5. Experimental data for the relative particle area, porosity and density of kaolinite clusters reported in the literature.

3.3 Effect of Simulation Time—Aggregated Particle Size and Structure

As indicated in section 3.1, the aggregated particle structures/clusters may continue to grow after 10 ns of simulation at pH 5. Thus, the effect of simulation time on the aggregated particle structures is presented in this section. Figure 7 (A) shows a snapshot of kaolinite particles at pH 5 after simulation for 20 ns and Figure 7 (B) represents the C.M. of kaolinite particles as well as aggregated particle structure identification (by color). A snapshot of the results of simulation extended to 30 ns is shown in Figure 8. As shown in Figure 7 and Figure 8, more complex aggregated particle structures, similar to the “card-house” structure, were developed with increasing simulation time. The results have confirmed that the aggregation of particles continued with increasing simulation time without reaching an equilibrium state.

Figure 7. (A) Brownian dynamics simulation snapshot of 1000 kaolinite particles at pH 5 after 20 ns simulation time (B) Representation of the center of mass (C.M.) of kaolinite

particles and aggregated particle structure identification (by color) at pH 5 after 20 ns simulation time.

Figure 8. (A) Brownian dynamics simulation snapshot of 1000 kaolinite particles at pH 5 after 30 ns simulation time (B) Representation of the center of mass (C.M.) of kaolinite particles and aggregated particle structure identification (by color) at pH 5 after 30 ns simulation time.

The aggregated particle structure size distributions as represented by the number of particles per aggregate structure at pH 5 are presented in Figure 9 as a function of simulation time (10ns, 20ns, and 30ns). A total of 47 aggregated particle structures were observed for 10 ns simulation time, and a total of 31 aggregated particle structures existed after 20 ns simulation time. The aggregated particle structures continued to coalesce and only 23 clusters remained after 30 ns simulation time. The surface areas of the aggregated kaolinite structures after 10 ns, 20 ns, and 30 ns simulation times were $258,865 \text{ \AA}^2$, $236,674 \text{ \AA}^2$, and $227,083 \text{ \AA}^2$. The volumes of the aggregated particle structures were computed as $928,776 \text{ \AA}^3$, $911,854 \text{ \AA}^3$, and $897,382 \text{ \AA}^3$. With increased simulation time both the surface area and the volume of the aggregated particle structures decreased slowly, which is additional evidence indicating that the aggregated particle structures continued growing and compacting.

Representative aggregated particle structures after simulation of 10 ns, 20 ns, and 30 ns are shown in Figure 6, Figure 10 and Figure 11. The surface area of typical aggregated particle structures and the surface area of the silica surface and the alumina surface are presented in Table 3, Table 6 and Table 7. Although the growth of the aggregated particle structures resulted in larger surface areas of individual particle structures with increased simulation time, the percent of the silica surface and the alumina surface did not change with increasing simulation time. The constant percent of

the silica/alumina surface area implied the interaction mode of kaolinite particles, namely alumina face to silica face interaction combined with alumina face to edge surface, was not a function of simulation time.

The above analysis of the simulation results indicates that the growth of the aggregated particle structures continued with increased simulation time, although the growth rate decreased. In addition, the results also suggest that although some of the small aggregated particle structures disappeared, they were combined or reorganized into larger aggregated particle structures. Generally speaking, 10 ns is long enough for traditional molecular dynamics simulation to reach an equilibrium state, however, the aggregated particle structures continually grew and the equilibrium state was not achieved in this study. In fact, a typical particle aggregation phenomena takes hours to reach a steady state, and in some circumstances, this steady state may not be able to be achieved in a reasonable time (days) (Likos and Lu 2001). To compute a simulation for hours would require a very powerful computer workstation and take months, even years, which is beyond the scope of this research.

Figure 9. (A) The aggregated particle structure size distribution for 10 ns simulation time (B) The aggregated particle structure size distribution for 20 ns simulation time (C) The aggregated particle structure size distribution for 30 ns simulation time.

Figure 10. Representation of typical aggregated particle structures formed at pH 5 after 20 ns simulation time. The aggregated particle structures were filled with volumetric solids by the EDTsurf method. The pink surfaces represent the silica face surfaces of the kaolinite particles, and the cyan surfaces represent the alumina face surfaces of the kaolinite particles.

Figure 11. Representation of typical aggregated particle structures formed at pH 5 after 30 ns simulation time. The pink surfaces represent the silica face surfaces of the kaolinite particles, and the cyan surfaces represent the alumina face surfaces of the kaolinite particles.

Table 6. Surface areas of typical aggregated particle structures after simulation for 20 ns and the surface areas of the silica and alumina surfaces. The particle structure number corresponds to the number labeled in Figure 10.

Table 7. Surface areas of typical aggregated particle structures after simulation for 30 ns and the surface areas of the silica and alumina surfaces. The aggregated particle structure number corresponds to the number labeled in Figure 11.

3.4 Validation of Cluster Structure

Direct examination of clusters was done using scanning electron microscopy with a WETSEM capsule. A small amount (~15 μ l) of kaolinite suspension (~50wt%) was injected into WETSEM capsules for SEM imaging at high vacuum. The electrons penetrated the specially designed membrane of the WETSEM capsule and the image of the wet kaolinite clusters underneath the membrane was acquired. The kaolinite face to face interaction and face to edge interaction are observed in Figure 12 (A), forming complex clusters in the suspension at low pH (pH 4.3).

Note that the gray-level variation in contrast of the particles was attributed to the energy decay when the electrons penetrated the water suspension, although the bright white section of the suspension may have dehydrated. An image with higher magnification could not be achieved due to the difficulty of imaging in water with SEM. In spite of frustration during the experiments, the complex cluster structure was observed at low pH and open water regions in the cluster structures were evident. The cluster size varied from 2 μ m to 15 μ m. In contrast to the results at pH 5, the particles were well-dispersed and suspended at pH 8 as shown in Figure 12 (B). In summary, the experimental results were in good agreement with the simulation results.

Figure 12. SEM images of kaolinite suspension in WETSEM cells at pH 4.3 (A) and pH 8.1 (B).

4. Summary and Conclusions

A new coarse grained model was developed for the simulation of anisotropic kaolinite particle interactions. Based on AFM experimental results, electrostatic and van der Waals forces acting on kaolinite particle surfaces were considered for simulation using a coarse grained model. Results have shown that at low pH (pH 5) large aggregated particle structures were formed by particle stacking as a result of alumina face to silica face interaction and alumina face to edge surface interaction, resulting in 10% more silica face surfaces exposed at the aggregated particle structure surface. In this regard, the exposed surfaces of the aggregated particle structures were more negatively charged. The cluster structure was discussed, analyzed, and shown to contain 48.4 vol% solids in the cluster.

The simulation time has been found to be an important factor which influences the aggregated particle structure/cluster structure. The aggregation of kaolinite particles continued with increased simulation time, but the growth rate of the aggregated particle structures decreased with time of simulation.

Finally experimental validation of the cluster structure was accomplished by SEM imaging with a WETSEM capsule. The experimental results revealed an open structure of the clusters at low pH with face to face stacking and face to edge interactions observed. The dispersed state of the kaolinite suspension at high pH was verified by SEM imaging as well. The experimental results confirmed the results obtained by simulation.

The findings from the simulation study will be an important consideration in kaolinite flotation and sedimentation. Particularly, it is believed that the strong aggregation of kaolinite particles at low pH accounts for the high flotation recovery of kaolinite from bauxite ore at low pH with a primary amine collector. In addition, at low pH ~10% more of the silica face surfaces of kaolinite are exposed in the clusters than alumina face surfaces, which facilitates amine collector adsorption and creation of a hydrophobic surface state for the kaolinite clusters. In conclusion, the results from this study help to explain the flotation of kaolinite and provide a foundation for the further development of flotation technology.

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Table 1. The surface charge density of silica and alumina surfaces at 1mM KCl used in the simulation.

pH	Surfaces	Surface Charge Density
5	Silica Surface	-2.0e/sphere
	Alumina Surface	0.5e/sphere
8	Silica Surface	-1.8e/sphere
	Alumina Surface	-1.3e/sphere

Table 2. Number of particles and their corresponding particle size in the simulation.

# of spheres on the side of a hexagon layer	7	6	5	4	3
# of spheres in one particle	254	182	122	74	20
# of particles in the simulation system	100	200	400	200	100

Table 3. Surface areas of typical aggregated particle structures after simulation of 10 ns, and areas of the silica and the alumina surfaces in each particle structure. The percent of each surface area (silica and alumina) for the particle structures is listed together with the average of the six particle structures. The particle structure number corresponds to that labeled in Figure 6.

Particle Structure Number	Surface Area of the Particle Structure ($\text{\AA}^2$)	Area of Silica Surface ($\text{\AA}^2$)	Area of Alumina Surface ($\text{\AA}^2$)	% of Silica Surface	% of Alumina Surface
1	22,377	12,408	9,969	55.4%	44.6%
2	14,258	7,716	6,541	54.1%	45.6%
3	10,900	5,965	4,935	54.7%	45.3%
4	10,671	5,917	4,755	55.4%	44.6%
5	10,446	5,775	4,672	55.3%	44.7%
6	9,304	5,060	4,244	54.4%	45.6%
Average	/	/	/	54.9%	45.1%

Table 4. Volume of each cluster, volume for the cluster enveloped by an ellipsoid, and the cluster aspect ratio. The percent solids for each cluster was determined from the ellipsoid volume.

Cluster Number	Volume ($\text{\AA}^3$)	Ellipsoid Volume ($\text{\AA}^3$)	Aspect Ratio	% Solids
1	85,449	483,619	2.07	17.7%
2	54,961	163,708	1.59	33.6%
3	42,071	110,323	1.42	38.1%
4	37,669	143,116	1.16	26.3%
5	38,172	157,128	1.49	24.3%
6	35,261	109,395	1.47	32.2%
7	34,004	108,393	1.30	31.4%
8	32,780	125,736	1.44	26.1%
9	31,688	122,770	1.21	25.8%
10	31,001	74,272	1.53	41.7%
11	24,807	61,501	1.52	40.3%
12	24,607	56,260	1.33	43.7%
13	22,006	59,099	1.54	37.2%
14	20,985	55,427	1.68	37.9%
15	20,525	39,312	1.39	52.2%
16	22,511	43,056	1.15	52.3%
17	20,065	37,740	1.33	53.2%
18	16,639	36,691	2.14	45.3%
19	18,347	33,920	1.16	54.1%
20	13,446	28,956	1.23	46.4%
21	12,815	22,987	1.48	55.7%
22	13,520	28,454	1.11	47.5%
23	12,355	33,430	1.53	37.0%
24	12,459	27,846	1.32	44.7%
25	11,270	24,916	1.33	45.2%
26	11,081	28,654	1.31	38.7%
27	10,671	24,113	1.41	44.3%
28	10,720	18,316	1.32	58.5%
29	9,314	19,634	1.45	47.4%
30	11,387	21,902	1.17	52.0%
31	8,580	20,592	2.05	41.7%
32	9,116	17,846	1.82	51.1%
33	8,397	13,978	1.90	60.0%
34	7,890	15,007	1.42	52.6%
35	9,508	13,057	1.15	72.8%
36	7,815	14,443	1.14	54.1%
37	5,917	11,457	1.42	51.6%
38	6,413	10,025	1.62	64.0%
39	6,910	9,140	1.00	75.6%
40	5,287	6,523	2.29	81.1%

41	5,464	12,630	1.34	43.3%
42	3,952	5,700	2.07	69.3%
43	4,488	6,490	1.30	69.2%
44	2,935	4,018	1.44	73.0%
45	2,543	4,210	1.44	60.4%
46	2,314	4,324	1.22	53.5%
47	419	598	1.16	70.2%
Average	/	/	1.45	48.4%

Table 5. Experimental data for the relative particle area, porosity and density of kaolinite clusters reported in the literature.

pH	Relative Particle Area (%)	Porosity (%)	Density (g/cm ³)	Reference
4	/	90	/	(Zbik et al. 2008)
8	/	30	/	(Zbik et al. 2008)
~6	8.64	/	2.0	(Du et al. 2009)
~6	/	90-95	1.05-1.10	(Likos and Lu 2001)

Table 6. Surface areas of typical aggregated particle structures after simulation for 20 ns and the surface areas of the silica and alumina surfaces. The particle structure number corresponds to the number labeled in Figure 10.

Particle Structure Number	Surface Area of the Particle Structure (Å ²)	Surface Area of Silica Surface (Å ²)	Surface Area of Alumina Surface (Å ²)	% of Silica Surface	% of Alumina Surface
1	42552	23104	19449	54.3%	45.7%
2	20082	10983	9100	54.7%	45.3%
3	19501	10867	8635	55.7%	44.3%
4	18126	10052	8074	55.5%	44.5%
5	12687	6798	5890	53.6%	46.4%
6	12064	6676	5388	55.3%	44.7%
Average	/	/	/	54.9%	45.1%

Table 7. Surface areas of typical aggregated particle structures after simulation for 30 ns and the surface areas of the silica and alumina surfaces. The aggregated particle structure number corresponds to the number labeled in Figure 11.

Particle Structure Number	Surface Area of the Particle Structure ($\text{\AA}^2$)	Surface Area of Silica Surface ($\text{\AA}^2$)	Surface area of alumina surface ($\text{\AA}^2$)	% of Silica Surface	% of Alumina Surface
1	39775	21507	18268	54.1%	45.9%
2	32718	17772	14946	54.3%	45.7%
3	30435	16758	13676	55.1%	44.9%
4	22612	12495	10116	55.3%	44.7%
5	12122	6631	5491	54.7%	45.3%
6	10780	6034	4745	56.0%	44.0%
Average	/	/	/	54.9%	45.1%

Figure 1. Crystal structure of kaolinite. Red: Oxygen; Yellow: Silicon; Purple: Aluminum; White: Hydrogen.

Figure 2. Stairstep card-house fabric of aggregated kaolinite particles (O'Brien 1971).

Figure 3. Coarse grained model for kaolinite particles (A) Top view (B) Side view. Cyan spheres represent the alumina face surface of the kaolinite particle, and pink spheres represent the silica face surface of the kaolinite particle.

Figure 4. (A) Brownian dynamics simulation snapshot of 1000 kaolinite particles at pH 5 after 10 ns simulation time; (B) snapshot of 1000 kaolinite particles at pH 8 after 10 ns simulation time. Pink spheres represent the silica face surfaces of kaolinite particles, and cyan spheres represent the alumina face surfaces of kaolinite particles.

Figure 5. (A) Representation of the center of mass (C.M.) of kaolinite particles and aggregated particle structure identification (by color) at pH 5 after 10 ns simulation time (B) Representation of the C.M. of kaolinite particles and aggregated particle structure identification (by color) at pH 8 after 10 ns simulation time.

Figure 6. Representation of typical aggregated particle structures formed at pH 5 after 10 ns simulation time. The particle structures were filled with volumetric solids by the EDTsurf method. The pink surfaces represent the silica face surfaces of the kaolinite particles, and the cyan surfaces represent the alumina face surfaces of the kaolinite particles.

Figure 7. (A) Brownian dynamics simulation snapshot of 1000 kaolinite particles at pH 5 after 20 ns simulation time (B) Representation of the center of mass (C.M.) of kaolinite particles and aggregated particle structure identification (by color) at pH 5 after 20 ns simulation time.

Figure 8. (A) Brownian dynamics simulation snapshot of 1000 kaolinite particles at pH 5 after 30 ns simulation time (B) Representation of the center of mass (C.M.) of kaolinite particles and aggregated particle structure identification (by color) at pH 5 after 30 ns simulation time.

Figure 9. (A) The aggregated particle structure size distribution for 10 ns simulation time (B) The aggregated particle structure size distribution for 20 ns simulation time (C) The aggregated particle structure size distribution for 30 ns simulation time.

Figure 10. Representation of typical aggregated particle structures formed at pH 5 after 20 ns simulation time. The aggregated particle structures were filled with volumetric solids by the EDTsurf method. The pink surfaces represent the silica face surfaces of the kaolinite particles, and the cyan surfaces represent the alumina face surfaces of the kaolinite particles.

Figure 11. Representation of typical aggregated particle structures formed at pH 5 after 30 ns simulation time. The pink surfaces represent the silica face surfaces of the kaolinite particles, and the cyan surfaces represent the alumina face surfaces of the kaolinite particles.

Figure 12. SEM images of kaolinite suspension in WETSEM cells at pH 4.3 (A) and pH 8.1 (B).

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Aggregated Particle Structure Size Distribution for 10 ns Simulation (A)

Aggregated Particle Structure Size Distribution for 20 ns Simulation (B)

Figure 9. (A) The aggregated particle structure size distribution for 10 ns simulation time (B) The aggregated particle structure size distribution for 20 ns simulation time (C) The aggregated particle structure size distribution for 30 ns simulation time.

Figure 10. Representation of typical aggregated particle structures formed at pH 5 after 20 ns simulation time. The aggregated particle structures were filled with volumetric solids by the EDTsurf method. The pink surfaces represent the silica face surfaces of the kaolinite particles, and the cyan surfaces represent the alumina face surfaces of the kaolinite particles.

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A

Face to Face
Interaction

Face to Edge
Interaction

7/21/2014	curr	HV	WD	mag	det	HFW	30 μm
11:45:18 AM	0.31 nA	15.0 kV	6.7 mm	2 000 x	ETD	153 μm	Ph 4.3

Figure 12. SEM images of kaolinite suspension in WETSEM cells at pH 4.3 (A) and pH 8.1 (B).