INFLUENCE OF AGGREGATE STRUCTURE ON SUSPENSION YIELD STRESS: A NUMERICAL STUDY
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ABSTRACT
This study theoretically examined the effect of aggregate structure on the suspension yield stress. The aggregation process of colloidal particles was simulated using the discrete element model (DEM) combined with the well-known DLVO theory. The predicted aggregate structural characteristics, namely the coordination number, and inter-particle forces were then used in a modified version of the Flatt and Brown mechanistic model [J. Am. Ceram. Soc. 89 (2006) 1244-1256] to calculate the corresponding suspension yield stress. The effect of key parameters such as solid volume fraction, suspension pH and ionic strength on the aggregate structure and hence the yield stress of the suspension was investigated.

The results showed that the yield stress increased significantly under conditions that were favourable for formation of complex net-like aggregate structures, such as high solid volume fractions, pH values near the iso-electric point, and high ionic strengths. The suspension yield stress exhibited a power law dependency on the solid volume fraction. The interconnected network structure developed at high solid volume fractions was found to be the major contributing factor to the observed high suspension yield stress. A decrease in the number of bonds and the mechanical bonding strength of the aggregate structure was found to be responsible for the smaller suspension yield stress as the particle-particle repulsion becomes significant. Satisfactory agreement was obtained between simulation results and the published experimental data.

Keywords: Aggregate structure, Coordination number, Suspension yield stress, DEM, DLVO, Numerical simulation.

INTRODUCTION
Yield stress is an important rheological characteristic of aggregated suspensions, as it dictates the input power-load to render the suspension flowable. In aggregated suspensions, the yield stress is a mechanical rigidity exhibited by the space filling particulate network that is formed due to interactions between colloidal particles. It is therefore closely related to structural properties of the particulate network, in terms of the strength of bonds between particles and the number of bonds that need to be broken. The bonding strength is controlled by inter-particle forces such as electrostatic, van der Waals, and/or steric and other more complex forces, which in turn are controlled by solution conditions and the particle surface, such as solution pH and ionic strength. The number of bonds depends on the network structural factors and particle parameters such as size and size distribution, shape, and volume fraction (Franks, 2002). Various theoretical models have been reported for the prediction of suspension yield stress. Generally, these models can be classified according to the calculation approaches into two categories. The first category predicts suspension yield stress based on the tensile strength of a bed of particles, where the second approach is based on the force balance on primary particles, mainly between inter-particle forces and shear stress.
Rumpf (1962) carried out the pioneering research in this field predicting the suspension yield stress by equating the tensile strength of a bed of mono-sized particles to the number of particle bonds per unit area and the bonding strength. Later, Kapur et al. (1997) modified the equation of Rumpf (1962) by incorporating the contribution from particle size poly-dispersity. However, the model was only valid in situations where the net electrical double layer (EDL) repulsive forces between particles were zero, i.e. at the iso-electric point (IEP). Scales et al. (1998) extended Kapur’s model to include the effect of particle-particle repulsion using the well-known DLVO theory. Flatt & Bowen (2006) developed a theoretical model (i.e. YODEL) based on the force balance analysis on a pair of bonding particles. The two-particle yield stress was then extrapolated into the overall suspension yield stress, and a subsistence probability was introduced to represent the fraction of specific system configurations, on which the forces were balanced. Overall better predictions were obtained using the force balance approach.

Generally, the above approaches rely on the accurate prediction of inter-particle forces and the aggregate structure. However, these parameters are often estimated based on simplifying assumptions and experimental correlations. Flatt & Bowen (2006) assumed a linear relationship between the maximum coordination number and solid volume fraction to predict the aggregate structure, while Kapur et al. (1997) and Scales et al. (1998) assumed an exponential relationship between the minimum inter-particle separation distance and the volume fraction of the solids to determine the inter-particle forces. Some of these simplifying assumptions have been challenged by other researchers (e.g. Zhou et al. (1999) found that inter-particle forces were not volume fraction dependent), while certain simplifications continued to be used due to lack of reliable data (e.g. Flatt & Bowen’s model ignores the EDL repulsive force in the absence of reliable data on inter-particle separation distances). Such simplifications hence limit the application of the yield stress models.

In this study, we employed the DEM technique to obtain a more realistic prediction of the aggregate structure and inter-particle forces. The DEM simulation results were then used in a modified version of the Flatt & Bowen yield stress model. Various forces, such as inter-particle forces, Brownian random force, contact forces, and buoyancy force were considered to simulate the motion of colloidal particles. The capability of the proposed method in predicting suspension yield stress was examined by altering key parameters, such as solid volume fraction, suspension pH and ionic strength. The predicted yield stress results were then compared with the published experimental data.

MATHEMATICAL MODEL

The mathematical model consists of two sequential parts: the first part involves simulating the aggregation process and predicting the aggregate structure and inter-particle forces using the DEM technique; the second part involves using the DEM simulation results as input data for a modified version of the Flatt & Bowen model (2006) to calculate suspension yield stress.

DEM simulation

In DEM simulation, each solid particle is considered individually, thus accounting for its dynamics due to the complex particle-particle and particle-fluid interactions (Cundall & Strack, 1979). The detailed information regarding the particle motion is captured at each time step. The translational and angular motion of single particles are calculated based on Newton’s equation of motion,
\[ m_p \frac{dv_p}{dt} = \sum f_p \] (1)

\[ I_p \frac{dw_p}{dt} = \sum M_p \] (2)

In Eq. (1), \( m_p \) and \( v_p \) are mass and translational velocity of the particle, respectively; \( f_p \) is the forces imposed on the particle. In Eq. (2), \( I_p \) and \( w_p \) are angular inertia and angular velocity, respectively; \( M_p \) is the torques exerted on the particle.

The major forces have been considered including surface force \( f_s \), contact force \( f_c \), Brownian random force \( f_B \), fluid drag force \( f_d \), buoyancy force \( f_b \) and the gravity \( G \). The torques comprises the components caused by the tangential contact force and by the rolling friction. The developed equations for the forces and torques have been detailed previously (Peng et al., 2010a, 2010b). Here, only inter-particle forces are outlined

**DLVO inter-particle forces**

In the absence of additives such as polymeric dispersants and coagulants, van der Waals and EDL forces are considered to be dominant forces in colloidal suspensions (Liang et al., 2007). The effect of these forces is commonly modelled using the well-known DLVO theory, which is the algebraic summation of van der Waals attractive force, \( f_{vdw} \) and EDL repulsive force, \( f_{ele} \). For two spherical particles, \( i \) and \( j \), these forces can be expressed as:

\[ f_{vdw} = - \frac{A_H (4\pi r_i r_j)^3}{6 s_{ij}} \left( s_{ij}^2 - (r_i + r_j)^2 \right) \times \left[ s_{ij}^2 - (r_i + r_j)^2 + 4rr_j \right] \] (3)

\[ f_{ele} = 64\pi\varepsilon_c\varepsilon_0k \left( \frac{RT}{zF_c} \right)^2 \times \tanh \left( \frac{zF_c\zeta_i}{4RT} \right) \times \tanh \left( \frac{zF_c\zeta_j}{4RT} \right) \times \frac{rr_i}{r_i + r_j} e^{-\kappa h_{ij}} \] (4)

where, \( h_{ij} \) is the surface separation distance, \( s_{ij} \) the centre-to-centre distance between the two particles, \( A_H \) the Hamaker constant, \( \kappa \) the Debye-Huckel parameter, \( F_c \) the Faraday constant, \( z \) the valence of the background electrolyte, \( \varepsilon_c \) the dielectric constant of the medium, \( \varepsilon_0 \) the permittivity of vacuum, and \( R \) the gas constant; \( \zeta_i \) and \( \zeta_j \) denote the zeta-potentials of the particles. Johnson-Kendall-Robert’s adhesive model (Hong et al., 1998) is commonly applied to avoid numerical singularity in Eq.(3).

**Suspension yield stress model**

In Flatt & Bowen’s model (2006), suspension yield stress is directly related to the number of bonds between particles. The force balance is carried out on a pair of bonding particles in order to represent the whole system. Each pair of the bonding particles is considered to behave as a new individual particle with a larger effective volume than the sum of the two original particles, as shown in Fig. 1.

The larger effective volume of the truncated cone of two bonding real particles leads to an increase in the solid volume fraction from \( \Phi \) to \( \Phi^* \). As aggregation proceeds, \( \Phi^* \) will continue increasing until it reaches \( \Phi_{max} \), which is the maximum packing density of the specific powder. When \( \Phi^* = \Phi_{max} \), the suspension is considered to yield (Flatt & Bowen, 2006) and the forces imposed on particles should be balanced. The force balance in the direction of the shear stress with several simplifying assumptions gives rise to an
Fig. 1: Truncated cone model to account for the increment of solid volume fraction as a result of the substituting new larger particle.

The equation for the yield stress of the colloidal system:

\[
\tau_y = \frac{12}{\pi V_d} \left( \phi - \phi_0 \right) \frac{m}{\phi_{\text{max}}} \sum_{k=1}^{m} \sum_{l=1}^{m} f_{s,kl} \frac{\Delta V_{kl}}{r_k^2 + r_l^2}
\]  

(5)

where, \( f_{s,kl} \) and \( C_{n,kl} \) are inter-particle forces and the coordination number between two kinds, \( k \) and \( l \), of particle sizes, and are calculated based on either assumptions or empirical formulas.

Since we are using DEM approach we are able to track each particle transiently, and hence the specific complex structural properties of fractal aggregates and particle interactions are known at any given time. The output data from the simulation, in particular the inter-particle forces between each pair of bonding particles and the coordination number of each particle, can be directly used to predict the suspension yield stress by the following equation,

\[
\tau_y = \frac{12}{\pi V_d} \left( \phi - \phi_0 \right) \frac{m}{\phi_{\text{max}}} \sum_{i=1}^{m} \sum_{j=1}^{m} f_{s,ij} \frac{\Delta V_{ij}}{r_i^2 + r_j^2}
\]  

(6)

where \( f_{s,ij} \) is inter-particle forces between particle \( i \) and particle \( j \); \( C_{n,i} \) is the coordination number of particle \( i \); the summation term includes the inter-particle forces of each pair of bonding particles, calculated based on their physical positions. The above approach enables a more realistic description of inter-particle forces and coordination number based on the aggregate structure that is formed under basic physicochemical laws, making it applicable for a variety of systems of different solution properties (e.g. pH and ionic strength) and particle parameters (e.g. shape, size and size distribution).

### NUMERICAL SIMULATION

![Graph showing particle size distribution](image)

Fig. 2: Particle size distribution.

A square two-dimensional (2D) domain was simulated to save the computation time and gain an insight into the effect of aggregate structure on the suspension yield stress. The
2D particle packing fraction was calculated as the total particle volume divided by the volume of the pseudo-3D space that has a depth of particle diameter. The particles were randomly introduced into the computational domain at \( t = 0 \)s of calculation. A minimum initial separation distance \( (h^*_{i=0} = \chi_{p}p) \) was chosen to guarantee the even distance between particles. The size distribution of primary particles is shown in Fig. 2. Periodic boundary conditions were used for all sides of the domain to minimise computational requirements and allow us to simulate a small part of the large system to represent the overall behaviour. A cut-off interaction distance, equal to the particle radius, beyond which the DLVO force was negligible, was chosen to minimise the computational time. The calculation parameters are listed in Tab. 1.

<table>
<thead>
<tr>
<th>Tab. 1: Calculation parameters</th>
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<tbody>
<tr>
<td><strong>Liquid:</strong></td>
</tr>
<tr>
<td>Concentration, ( C_e )</td>
</tr>
<tr>
<td>Dielectric constant, ( \varepsilon_m )</td>
</tr>
<tr>
<td>Conductivity, ( \sigma_m )</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Ionic valence, ( z )</td>
</tr>
<tr>
<td>Temperature, ( T )</td>
</tr>
<tr>
<td><strong>Particle (( \alpha )-Alumina):</strong></td>
</tr>
<tr>
<td>Number of particle, ( N_p )</td>
</tr>
<tr>
<td>Density, ( \rho_p )</td>
</tr>
<tr>
<td>Mean size, ( d_p )</td>
</tr>
<tr>
<td>Restitution coefficient, ( e_{p,a} )</td>
</tr>
<tr>
<td>Spring stiffness, ( k )</td>
</tr>
<tr>
<td>Sliding friction coefficient, ( \mu_p )</td>
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<td>Rolling friction coefficient, ( \mu_f )</td>
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<td>Dielectric constant, ( \varepsilon_p )</td>
</tr>
<tr>
<td>Conductivity, ( \sigma_p )</td>
</tr>
<tr>
<td>Volume fraction, ( \Phi_s )</td>
</tr>
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</table>

**RESULTS AND DISCUSSION**

**Effect of solid volume fraction**

Fig. 3 shows the network structures of colloidal suspension formed at 0.26, 0.36, and 0.54 solid volume fractions. The coloured line connecting two bonding particles signifies the surface separation distance and implies the bonding strength of the network structure, where \( a \) is the harmonic average radius of two bonding particles \( i \) and \( j \), i.e.

\[
\frac{1}{a} = \frac{1}{r_i} + \frac{1}{r_j}
\]

Fig.3: Aggregate structure versus solid volume fraction (pH=9, \( C_e=0.01 \)M, \( t=1.7 \)s)
It can be seen that a complex and strongly bonded particulate network is formed at high solid volume fractions (Fig. 3(c)), where particles distribute in the domain with very short separation distances (i.e. the red lines). In dilute suspensions (Fig. 3(a)), while the strong bonds and the space filling network structure are also observed, aggregates are more isolated and the interstitial space in between them is very large. This simulated result of aggregate structure complies well with the experimental observation through the Confocal Laser Scanning Microscope by Stradener et al. (2004) and Campbell et al. (2005).

The quantitative analysis on the effect of solid volume fraction on suspension yield stress is shown in Fig. 4. As solid volume fraction increases, the suspension yield stress increases in power-law dependence. This trend has been observed experimentally by many researchers (Channell & Zukoski, 1997; Shih et al., 1999; Flatt & Bowen, 2006). The particulate network structure is considered to be the main contributing factor for such behaviour. As the solid volume fraction increases, the increased local particle number density accelerates the aggregation process. Complex interconnected network with multiple connection points is formed, as shown in Fig. 3. As a result, larger shear stress is entailed to overcome the bonding forces maintaining the network structure. In dilute suspensions, the strong bonds are also formed due to the dominant van der Waals attraction. However, due to fewer neighbouring particles and the increasing separation distance as aggregation proceeds, the aggregates formed are either apart from each other or connected by few joints, as shown in Fig. 3(a). Consequently, the overall bonding strength in dilute suspensions is weaker than that in concentrated suspensions.

Also shown in Fig. 4 is the experimental result by Zhou et al. (1999) under the same conditions. While the model describes the trend very well, it underestimates suspension yield stress at high solid volume fractions. The two dimensional (2D) simulation is thought to be the primary reason for the deviation. In dilute suspensions, the difference between 2D and 3D coordination numbers is rather negligible, since aggregates generally consist of few particles. However, in very high particles concentrations, the 3D coordination numbers are generally 1.5 – 2 times greater than that of 2D systems. Underestimating the coordination number leads to lower predicted values of suspension yield stress in concentrated suspensions. Moreover, the ideally spherical particle shape may be another important factor leading to the deviation. The actual particles are roughly equiaxed, more like “potatoes” than spheres, which will also contribute to the larger yield stress in the real (3D) space.

![Fig. 4: Suspension yield stress versus solid volume fraction (pH=9, C_e=0.01M, t=1.7s)](image-url)
**Effect of pH**

Fig. 5 demonstrates the effect of suspension pH on the aggregate structure. It can be seen that when suspension pH is away from the IEP of α-Alumina particles, i.e. at pH = 9.2 (Zhou et al., 1999), scattered aggregates are formed with very weak bonding strength (Fig. 5(a)). At these pH values, the EDL repulsive force is significant and consistently prohibits particles from approaching each other. That in turn leads to large separation distances (see the colour bar in Fig. 3), and aggregate structures with weak bonding strength are formed. Moreover, small sized particles are observed outside the aggregates. This is because small particles have more intense Brownian motion and appear more active. As a result, they readily bounce off under the pronounced particle-particle repulsion. As suspension pH comes closer to IEP (Fig. 5(c)), typical network structure is formed and all small particles fill in the space between the large ones.

![Fig. 5: Aggregate structure versus pH (Φs=0.3, Ce=0.01M, t=2.05s)](image)

Fig. 6 shows the dependence of suspension yield stress on pH. It can be seen that suspension yield stress increases as pH becomes closer to the IEP, and reaches the maximum at pH=9. At pH = 9, the net EDL repulsion is zero and the attractive van der Waals force is the dominant surface force, which results in the strong aggregation and the complex interconnected network of substantial mechanical strength. Similar results are reported by other researchers both experimentally and theoretically (e.g. Liddell, 1996; Scales et al., 1998; Zhou et al., 1999; Yan et al., 2000; Peng et al., 2010a). At pH values that are far away from IEP (e.g. at pH = 7 and 8), the repulsive force between particles becomes significant and resists particles from aggregating. Consequently, the number of bonds (i.e. the mean coordination number) of the suspension is smaller, as indicated in Fig. 7. Moreover, as shown in Fig. 5(a)-5(b), the suspension is partially aggregated with isolated aggregates of very weak bonding strength. Consequently, the

![Fig. 6: Suspension yield stress versus pH (Φs=0.3, Ce=0.01M, t=2.05s)](image)
yield stress is much smaller. The experimental results for suspension yield stress as a function of pH are also shown in Fig. 6 (Zhou et al., 1999). Good agreement is observed between the predicted yield stress and the measured data. This agreement further verifies the capability of the proposed method for the prediction of suspension yield stress over a wide range of suspension properties.

Fig. 7: Dependence of mean coordination number on pH ($\Phi_s=0.3$, $C_e=0.01$, $t=2.05s$)

**Effect of ionic strength**

Fig. 8 shows the particulate structure of colloidal suspensions under different ionic strengths at pH= 7. At very low ionic strength (Fig. 8(a)), no aggregates are observed. As the ionic strength increases (e.g. at 0.1 M), small aggregates are formed and scatter in the domain with the dominant separation distance staying in the middle range (see the colour bar in Fig.3). When $C_e$ increases further to 1 M, great difference is observed in the particulate structure, where typical network of strong bonding strength are formed.

Fig. 8: Aggregate structure versus ionic strength ($\Phi_s=0.3$, pH=7, $t=2.14s$)

Tab. 2 shows the predicted suspension yield stress as a function of ionic strength under pH = 7, pH = 8 and pH = 9, and the corresponding coordination number is shown in Fig. 9. The status of “non-yielded” indicates that the effective solid volume fraction (i.e. $\Phi^*$) has not reached the maximum packing fraction $\Phi_{max}$, and the suspension is considered not having a yield stress. Negligible influence of $C_e$ is observed when pH is in the vicinity of IEP (e.g. pH = 9), where the attractive van der Waals force that is independent of pH and ionic strength, is the monotonic driving mechanism for particle aggregation. However, at pH values away from IEP (i.e. pH = 7 and 8), the zeta potential on the particle surface is greater and the influence of ionic strength becomes
significant. At low ionic strengths, the large energy barrier between the particles keeps them away from each other and as a result, very few aggregates are formed (see Fig. 8(a)). All the primary particles are well dispersed with a near zero mean coordination number, as shown in Fig. 9. As the ionic strength increases, the thickness of the electrical double layer decreases, which in turn reduces the energy barrier between the two particles. Hence, it becomes much easier for particles to overcome the energy barrier and form aggregates. Accordingly, the mean coordination number increases rapidly.

After the ionic strength surpasses a critical value, referred to as the critical coagulation concentration (CCC) by Elimelech et al. (1995), the energy barrier completely vanishes and rapid aggregation occurs (e.g. in Fig. 8(c)). It is worth noting that the suspension yield stress and mean coordination number do not change very much after the CCC. This is because under the same suspension pH and solid volume fraction, the driving mechanisms of aggregation are the same and leads to very similar aggregate structure.

<table>
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<tr>
<th>pH</th>
<th>ionic strength (M)</th>
<th>suspension yield stress (Pa)</th>
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<tbody>
<tr>
<td>7</td>
<td>0.001 M</td>
<td>Non-yielded</td>
</tr>
<tr>
<td></td>
<td></td>
<td>94.70873</td>
</tr>
<tr>
<td>8</td>
<td>0.01 M</td>
<td>Non-yielded</td>
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<tr>
<td></td>
<td></td>
<td>88.79052</td>
</tr>
<tr>
<td>9</td>
<td>0.1 M</td>
<td>Non-yielded</td>
</tr>
<tr>
<td></td>
<td></td>
<td>78.96668</td>
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<tr>
<td>1 M</td>
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<tr>
<td></td>
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**CONCLUSION**

The DEM technique was employed to simulate the aggregation process of colloidal particles. The simulated aggregate structure was then used in a modified version of the Flatt & Bowen model to predict suspension yield stress. The effects of key parameters, e.g. solid volume fraction, suspension pH and ionic strength, were examined.

Complex and strongly bonded particulate network was formed at high solid volume fractions, whereas isolated aggregates connected by few joints are formed in dilute suspensions. As solid volume fraction increases, the suspension yield stress increases in power-law dependence, and the mean coordination number increases in a non-linear fashion. When suspension pH is away from IEP, scattered aggregates of very weak bonding strength are formed, and small sized particles are distributed outside the aggregates. As pH comes closer to IEP, typical network structure is formed and suspension yield stress increases. Negligible influence of the ionic strength is observed when pH is in the vicinity of IEP. However, at pH values away from IEP, aggregates
started forming and the coordination number increases rapidly as the ionic strength increases; after the ionic strength surpasses the CCC, rapid aggregation occurs and suspension yield stress reaches the maximum. Both suspension yield stress and coordination number do not change very much beyond the CCC. Good agreement was obtained between simulation results and the published experimental data.

REFERENCES


BRIEF BIOGRAPHY OF PRESENTER

Dr. Peng, Z., completed his PhD degree at the end of 2008 in Southeast University in China, and currently is working in the University of Newcastle in Australia, focusing on the packing and fluidisation behaviour of nanoparticles in microfluidic devices.