Collision efficiency factor for heteroaggregation: Extension to soft interactions

Aaron Olsen and George Franks
Centre for Multiphase Processes, The University of Newcastle, Callaghan, New South Wales 2308, Australia

Simon Biggs
Department of Process, Environmental and Materials Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom

Graeme J. Jameson
Centre for Multiphase Processes, The University of Newcastle, Callaghan, New South Wales 2308, Australia

(Received 13 March 2007; accepted 2 August 2007; published online 31 January 2008)

An improved model for the collision efficiency factor of clusters of oppositely charged spheres has been developed, which accounts for repulsive and attractive interactions that occur at a finite distance from the colliding species, i.e., the so-called “soft” interactions. Trends in measured optimum dosages for rapid aggregation with increasing Debye length (a decrease at particle size ratios between 0.3 and 1 and an increase at particle size ratios less than 0.3) are explained qualitatively by employing the modified collision efficiency model. Several observations from the literature, specifically the formation of stringlike aggregates at low ionic strength and the uneven optimum dosage requirements of particles of equal size, are also explained in view of the model presented.


I. INTRODUCTION

The rate of aggregate growth in an unstable system of particles is generally considered to be proportional to the number of binary collisions, per unit time and volume, resulting in adhesion, which for two species, i and j, is expressed as

\[ J_{ij} = K_{ij}N_iN_jE_{ij}, \]

where \( N_i \) and \( N_j \) are the number concentration of each species and \( K_{ij} \) is a second order collision rate constant, which takes into account the physical parameters of the system (particle size, temperature, etc.) as well as the transport mechanisms by which collisions are facilitated. The term \( E_{ij} \) is known as the collision efficiency factor and it is simply equal to the fraction of collisions that result in adhesion. It is apparent from Eq. (1) that maximization of the collision efficiency factor is important for optimizing the rate of aggregation.

In a previous paper, a geometric model was presented as the basis for quantifying the collision efficiency factor (\( E \)) for flocculation of oppositely charged particles (heteroaggregation). It was demonstrated that this model was capable of accurately predicting the optimum concentration of small particles to achieve the maximum aggregation rate of larger oppositely charged particles at high ionic strength (low Debye length). That is, an assumption of the model being that the interaction distance of the particles is small relative to the particle size.

Puertas et al.\(^3,4\) showed that for two species of equal sized, oppositely charged particles, the optimal relative number concentration of particles for maximum aggregation rate is one-half if the surface potential of both species is the same. This is in agreement with the collision efficiency model presented by Olsen et al.\(^2\). However, Puertas et al. found that if the surface potential of one species is lower than that of the other, a greater relative fraction of the less charged species is required to achieve the maximum aggregation rate. This change in optimum dosage should be due to a change in collision efficiency factor but the geometric model\(^2\) of \( E \) makes no allowances for variation in surface potential.

The work presented here attempts to modify the collision efficiency model presented previously\(^5\) to allow for soft interactions, i.e., particle interactions for which the Debye length is significant relative to the particle size. Correction factors are incorporated to account for interactions at a finite distance from the surface of the interacting species, and a number of trends observed from experiment and literature are explained qualitatively using the modified model.

II. THEORY

A. Background

The relationship to describe the collision efficiency factor for two aggregates (\( m \) and \( m' \)) composed of the same ratio of oppositely charged spherical particles (denoted as species 1 and 2) is\(^2\)

\[ aaron.olsen@bristol.ac.uk. 

Author to whom correspondence should be addressed. Tel.: +44(0)1173317156; Fax: +44(0)1179250612; Electronic mail: aaron.olsen@bristol.ac.uk.
\[
E_{nm'} = \left( \frac{\sum A_{m(1)} - \sum A_{m(1)}}{\sum A_{m(T)}} + \frac{\sum A_{m'(2)} - \sum A_{m'(2)}}{\sum A_{m'(T)}} \right) \\
\times \left( \frac{\sum A_{m(1)}}{\sum A_{m(T)}} + \frac{\sum A_{m'(1)}}{\sum A_{m'(T)}} \right),
\]

where, for example, \( \sum A_{m(2)} \) is the total area of a particle species 1 in an aggregate of species \( m \) exposed to collisions with particle species 2 in an aggregate \( m' \). For aggregate \( m \), these areas can be defined by the equations

\[
\sum A_{m(2)} = 4\pi R_1^2 - \frac{N_2}{N_1} a_{1(2)},
\]

\[
\sum A_{m(1)} = \frac{N_2}{N_1} (4\pi R_2^2 - a_{2(1)}),
\]

\[
\sum A_{m(1)} = 4\pi R_1^2 - \frac{N_2}{N_1} a_{1(1)},
\]

\[
\sum A_{m(2)} = \frac{N_2}{N_1} (4\pi R_2^2 - a_{2(2)}),
\]

and the total area in \( m \) exposed to a collision of any kind \( (\sum A_{m(T)} \) is the same as that exposed to a collision with a smaller particle,

\[
\sum A_{m(T)} = \sum A_{m(2)} + \sum A_{m(2)},
\]

where \( R \) is the radius of the particle species denoted by the subscript, \( N_2/N_1 \) is the relative number concentration of particles (particle species 1 and 2 are defined such that \( N_2/N_1 \) is greater than or equal to 1), and \( a \) is the area shielded from collision, the expressions for which are

\[
a_{1(2)} = a_{2(1)} = 4\pi \left( \frac{R_1 R_2}{R_1 + R_2} \right)^2,
\]

\[
a_{1(1)} = 2\pi R_1 \left( \frac{R_1 R_2}{R_1 + R_2} \right),
\]

and

\[
a_{2(2)} = 2\pi R_2 \left( \frac{R_1 R_2}{R_1 + R_2} \right).
\]

In some cases, the distance of closest approach of like-charged particles \( (D_{11} \) and \( D_{22} \) and the distance of furthest attraction of oppositely charged particles \( (D_{12} \) are sufficiently small relative to the size of the particles present that they can be approximated as zero. This is certainly the case for the results presented previously, aggregation being performed with a background electrolyte concentration of 0.01 mol L\(^{-1}\) KNO\(_3\), corresponding to an approximate Debye length \( (1/\kappa) \) of 3 nm. However, in many situations, this would not be the case and \( D_{11}, D_{22}, \) and \( D_{12} \) must be taken into consideration. Equation (2) will still be valid but the expressions for the relative exposed areas of each particle must take these distances into consideration.

**B. Model Modification**

Equations (3)–(10) assume that the electric double layer of each particle has no bearing on the effective area of each particle exposed to the possibility of attractive and repulsive collisions. Given that the overlap of like-signed double layers must result in repulsion of particles before contact is made (otherwise the system is inherently unstable), there must exist a distance of closest approach between such particles \( (D_{11} \) and \( D_{22} \) for large and small particles, respectively). Likewise, at some interparticle separation greater than zero \( (D_{12} \), particles of opposite charge will experience an attractive potential greater than the combined components of their kinetic energy directing the particles away from one another such that adhesion is ultimately inevitable.

In short, the collision radius of a particle may not necessarily be approximated as being equivalent to its physical radius. Rather, the collision radius is equal to the physical radius plus the appropriate interaction distance, \( D_{11}, D_{22}, \) or \( D_{12} \). Since these are the interparticle distances at which the probability of repulsion or attraction is unity, they should be included when calculating the areas exposed to such collisions for substitution into the collision area equations.

Figure 1 illustrates two dimensionally the manner in which the geometry of a particle system may be altered by the distances of closest approach and furthest attraction. It is assumed that these distances are constant for any collision between the same two particles, irrespective of orientation. Thus these distances trace a circular path around each particle in two dimensions (as demonstrated by the broken line
in Fig. 1). This assumption may break down in the region where oppositely charged particles meet, but given that this area is small relative to the total area of the particles, it should suffice as a reasonable approximation.

If the distances \( D_{11}, D_{22}, \) and \( D_{12} \) are known, it is possible to calculate the effective area of each particle exposed to attractive and repulsive collisions, as required for calculation of the collision efficiency factor. This is simply the total area less the area shielded from collisions, which in the case of attractive collisions, can be expressed as

\[
\sum A_{1(2)} = 4\pi(R_1 + D_{12})^2 - \frac{N_2}{N_1}a_{1(2)}
\]  

and

\[
\sum A_{2(1)} = \frac{N_2}{N_1}(4\pi(R_2 + D_{12})^2 - a_{2(1)}).
\]

The area shielded from collisions is given by the equation for a spherical cap, which for Eq. (11) is

\[
a_{1(2)} = 2\pi R_1 h_{1(2)},
\]

where \( h_{1(2)} \) is the distance to the edge of the sphere perpendicular to the plane, the value of which can be calculated using simple trigonometry. Applying the law of cosines for a right angle triangle we get the expression

\[
\cos \theta_{1(2)} = \frac{R_1 + D_{12} - h_{1(2)}}{R_1 + D_{12}}.
\]

Again, applying the law of cosines we get

\[
\cos \theta_{1(2)} = \frac{(2R_2 + D_{22})^2 - (R_1 + R_2 + D_{12})^2 - (R_1 + R_2)^2}{2(R_1 + R_2)(R_1 + R_2 + D_{12})}.
\]

Equating Eqs. (14) and (15) it can be shown that

\[
h_{1(2)} = (R_1 + D_{12}) \times \left[1 - \frac{(R_1 + R_2)^2 + (R_1 + R_2 + D_{12})^2 - (2R_2 + D_{22})^2}{2(R_1 + R_2)(R_1 + R_2 + D_{12})}\right].
\]

Equations (13) and (14) may be modified for Eq. (12) by simply interchanging the numerical subscripts (i.e., \( 1 \rightarrow 2 \) and \( 2 \rightarrow 1 \)) for each variable, remembering that \( D_{12} = D_{21} \).

The distances \( D_{11}, D_{22}, \) and \( D_{12} \) are difficult to determine (either from theory or by experiment) for interactions involving clusters of oppositely charged particles, so quantitative application of the proposed extension of the collision efficiency model is not readily achievable. To investigate the validity of the model it will be used to investigate qualitatively trends in optimum dosage with increasing Debye length.

### III. EXPERIMENT

#### A. Materials

All the water used is Millipore “Milli-Q Academic” grade de-ionized water. Suspensions were adjusted to \( \rho \text{H} 5 \) using analytical grade \( \text{HNO}_3 \) (Aldrich). An electrolyte concentration of 0.01 mol L\(^{-1} \) of analytical grade \( \text{KNO}_3 \) (Aldrich) was used in all experiments.

The particle systems used in all experiments were aqueous suspensions of cationic (amidine functionalized) and anionic (sulfate functionalized) polystyrene latex (PSL) particles (Interfacial Dynamics Corp., Eugene, OR). The concentration of these particles was varied as required to achieve the desired relative number concentration of anionic to cationic particles. In all cases, the cationic particles were the larger of the two species (310 nm) and a number of different sized smaller anionic particles were used.

The nominal number-averaged radius and coefficient of variance (CV) of each particle species, as quoted by the manufacturer, are presented in Table I. These values were confirmed by dynamic or small-angle static light scattering experiments (Malvern Zetasizer ZS and Malvern Mastersizer 2000).

The electrophoretic mobility of the PSL particles was measured (Malvern Zetasizer ZS) for the given conditions. The calculated zeta-potentials (\( \zeta \)), using the Smoluchowski equation, are presented in Table I.

#### B. Aggregation

The cationic particles and anionic flocculant particles used in each aggregation experiment were first diluted in separate containers to equivalent volumes. The volume fraction of the cationic PSL species was \( 1.25 \times 10^{-5} \), corresponding to an approximate number concentration of \( 1.83 \times 10^{10} \) m\(^{-3} \). This is within the range found to give negligible multiple scattering\(^2 \) for the static light scattering technique and is low enough to monitor aggregation rate with time. The concentration of flocculant was varied according to the requirements of the individual experiment.

The dilute particles and flocculant were combined in a 160 ml standard dimension mixing vessel A 10 s period of

<table>
<thead>
<tr>
<th>( R ) (nm)</th>
<th>%CV</th>
<th>( \zeta ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>310</td>
<td>3.1</td>
<td>+43</td>
</tr>
<tr>
<td>9.5</td>
<td>14.4</td>
<td>−49</td>
</tr>
<tr>
<td>21.5</td>
<td>17.1</td>
<td>−52</td>
</tr>
<tr>
<td>29</td>
<td>11.2</td>
<td>−42</td>
</tr>
<tr>
<td>40</td>
<td>8.3</td>
<td>−37</td>
</tr>
<tr>
<td>55</td>
<td>8.4</td>
<td>−40</td>
</tr>
<tr>
<td>75</td>
<td>5.3</td>
<td>−41</td>
</tr>
<tr>
<td>111.5</td>
<td>5.9</td>
<td>−43</td>
</tr>
<tr>
<td>152</td>
<td>7.9</td>
<td>−36</td>
</tr>
<tr>
<td>207.5</td>
<td>3.6</td>
<td>−45</td>
</tr>
</tbody>
</table>
initial mixing was applied using a six-blade Rushton impeller driven by an overhead stirrer at 150 rpm. This brief mixing period was intended to rapidly achieve an even distribution of particles and flocculant while having minimal effect on the flocculation process, thus preserving perikinetic conditions.

Aggregate growth was monitored using a Malvern Mastersizer 2000, a low-angle static light scattering instrument. Details of the light scattering experiments used are given in a previous publication. The aggregating system was transferred from the mixing vessel to the scattering cell of the Mastersizer 2000 by means of a peristaltic pump. The pump was connected in-line after the Mastersizer cell. A flow rate of $1.4 \times 10^{-3}$ s$^{-1}$ was maintained for 30 s to allow the flow cell to completely fill, at which time the pumping was discontinued and measurement of the light scattered by the sample was initiated.

### IV. RESULTS AND DISCUSSION

#### A. Measured optima: Similar sized particles ($0.3 < R_2/R_1 < 1$)

The measured optimum dosages for maximum aggregation rate for heteroaggregation of the similar sized anionic and cationic PSL particles from Table I are shown in Table II. The data shown are for electrolyte concentrations of $1 \times 10^{-2}$ and $1 \times 10^{-3}$ mol $L^{-1}$ KNO$_3$, corresponding to approximate Debye lengths of 3.0 and 30.0 nm, respectively. In the case of $R_2/R_1 = 0.36$, the optimum dosage is also shown for a background electrolyte concentration of $1 \times 10^{-3}$ mol $L^{-1}$ KNO$_3$, corresponding to an approximate Debye length of 9.6 nm.

As the ranges of attraction and repulsion are larger for the lower electrolyte concentrations, $D_{11}$, $D_{22}$, and $D_{12}$ will be significantly greater. It is apparent from Table II that accompanying the changes in these interaction distances, a small decrease in the optimum dosage is observed. The exception being $R_2/R_1 = 0.36$, where no change in optimum dosage is observed between $1 \times 10^{-2}$ and $1 \times 10^{-3}$ mol $L^{-1}$ KNO$_3$. However, a decrease is observed between $1 \times 10^{-2}$ and $1 \times 10^{-3}$ mol $L^{-1}$ KNO$_3$ but is counteracted by an increase between $1 \times 10^{-3}$ and $1 \times 10^{-4}$ mol $L^{-1}$ KNO$_3$.

From Derjaguin-Landau-Verwey-Overbeek theory the double layer interaction potential is proportional to the size of the interacting particles (assuming equivalent surface potential of each). Assuming that the kinetic energy of each particle in the system is the same, for similar sized particles, it is thus expected that $D_{11}$, $D_{22}$, and $D_{12}$ are all approximately equivalent. Calculation of $(N_2/N_1)_{opt}$ for equivalent values of $D_{11}$, $D_{22}$, and $D_{12}$ reveals only a slight reduction from that obtained if they were assumed to be zero. This is demonstrated in Fig. 2, which shows the predicted optima for a range of particle size ratios and values of $D_{11}$, $D_{22}$, and $D_{12}$.

The reduction in optimum dosage with increasing $D_{11}$, $D_{22}$, and $D_{12}$ is easily understood by extending each distance toward infinity. As each distance approaches infinity the finite size of each particle becomes negligible. The effective collision radius, and thus the exposed area of each particle, is approximately equivalent, such that the two species approximate identically sized particles and the optimum dosage thus tends toward unity, as observed.

The increase in optimum dosage in the case of $R_2/R_1 = 0.36$ between $1 \times 10^{-2}$ and $1 \times 10^{-4}$ mol $L^{-1}$ KNO$_3$ is contrary to the observations made for other particle size ratios as well as the predictions of the adjusted collision efficiency model. In such cases, the dissimilarity of particle size becomes important, as is explained in the following section.

#### B. Measured optima: Dissimilar sized particles ($R_2/R_1 < 0.3$)

Figure 3 shows the measured optimum dosages for particle size ratios below $R_2/R_1 = 0.17$ at $1 \times 10^{-3}$, $1 \times 10^{-4}$, and $1 \times 10^{-5}$ mol $L^{-1}$ KNO$_3$. These data are compared with the predictions of optimum dosage, neglecting double layer effects. Clearly there is a deviation from the predicted optima, increasing with both decreasing particle size ratio and decreasing electrolyte concentration. The observed effect of electrolyte concentration here is opposite to that seen for similar sized particles in Fig. 2, with the exception of $R_2/R_1 = 0.36$, between $1 \times 10^{-2}$ and $1 \times 10^{-4}$ mol $L^{-1}$ KNO$_3$ as already mentioned.

For systems of oppositely charged particles, at sufficiently high concentrations of the smaller species of particle (or the more populous in the case of identically sized particles), the close proximity of these particles on the surface of the larger particles may prevent contact between the latter. The number of particles required to achieve the blocking of

![Fig. 2. Predicted optimum dosage for size ratios between 0.3 and 1, assuming a constant distance of closest approach and attraction ($D=D_{11}=D_{22}=D_{12}$) and $R_1=310$ nm.](image_url)
large-large interactions (the critical blocking concentration) can be estimated using geometric relationships, given several assumptions: (i) an even distribution of small particles across the larger particle surface in a hexagonal arrangement (scanning electron micrographs presented by Harley et al. for adsorption of small PSL particles onto large particles show a remarkably even spacing) and (ii) rearrangement of adsorbed particles does not occur during collisions (a reasonable assumption as the lateral component of the repulsive force between adsorbed and colliding particles would not be as great as that between adsorbed particles). The critical blocking concentration for large-large interactions can then be expressed as

\[
\left( \frac{N_2}{N_1} \right)_{b(\text{min})} = 2 - 4\pi \\
\times 6\sin^{-1}\left( \frac{2R_1^2 - 2R_1R_2 - R_2^2}{4R_1^2 + 2R_1R_2 + R_2^2} \right) - \pi^{-1},
\]

the derivation for which is given in the Appendix.

The solution to Eq. (17) over a range of particle size ratios is shown in Fig. 3. Comparison with the optimum dosage predicted by Eq. (2) shows a distinct correlation in trend below a size ratio of approximately 0.3. Above this size ratio the optimum dosage follows an approximate negative square trend as a function of particle size ratio. If it is assumed that the repulsive area of interaction on any given particle is approximately the same as the attractive area of interaction (for example, \(\Sigma A_{m1(1)} = \Sigma A_{m1(2)}\)), Eq. (2) simplifies to

\[
\left( \frac{N_2}{N_1} \right)_{b(\text{min})} = 2 - 4\pi \left[ 6\sin^{-1}\left( \frac{3D_{11}(D_{11} + 4R_1) + 4(2R_1^2 - 2R_1R_2 - R_2^2)}{3D_{11}(D_{11} + 4R_1) + 4(2R_1^2 + 2R_1R_2 + R_2^2)} \right) - \pi \right]^{-1},
\]

where the sum of the two multiplicative terms must be unity. The maximum value of \(E_{\text{mm}}\) from this equation must be 1/2, for the case where the total attractive area of small particles in each aggregate is equal to that of the large particle. This is similar to the half surface coverage condition of the La Mer–Smellie collision efficiency model. Substituting Eqs. (3) and (5) into Eq. (18) and rearranging to make \(N_2/N_1\), the subject yields

\[
\left( \frac{N_2}{N_1} \right)_{\text{opt}} = \left( \frac{N_2}{N_1} \right)_{b(\text{min})} = \left( \frac{R_2}{R_1} \right)^{-2}.
\]

That is, the optimum number ratio of oppositely charged particles for maximum steady-state aggregation rate should be approximately equal to the inverse square of the particle size ratios, as seen at size ratios above 0.3 in Fig. 3. While it is expected that Eq. (19) becomes increasingly inaccurate with increasing difference in particle sizes (due to the increasing inaccuracy of the assumption of equivalent repulsive and attractive areas on the same particle), the inflection in the theoretical trend in optimum dosage below a size ratio of 0.3 seen in Fig. 3 is clearly the result of large-large blocking.

If large-large interactions are blocked, the only possible particle-particle interactions are small large and small small, these interactions being attractive and repulsive respectively. Repulsive interactions are minimized provided there is the minimum number of small particles required to prevent contact between larger particles. The minimum number of particles required to achieve blocking is then the optimum condition for maximum \(E_{\text{mm}}\) provided no higher value can be attained below the critical blocking concentration. The discrepancy between the optimum dosage and critical blocking concentration is due to the omission of the correction factor for overlapping shielded areas when calculating the former. As such, comparison of the measured optima should be made with the curve for the critical blocking concentration.

For smaller particle size ratios \((R_2/R_1 < 0.3)\) the blocking of interactions between large particles due to the close proximity of smaller adsorbed particles determines the optimum dosage for maximum aggregation rate. If the distance of closest approach of the large particles is greater than zero, as will increasingly be the case with decreasing electrolyte concentration, this distance must be taken into consideration when determining the critical blocking concentration. Applying simple trigonometry (Appendix) the adjusted critical blocking concentration is given by the expression

\[
E_{\text{mm}} = 2 \left( \frac{\Sigma A_{m1(2)}}{\Sigma A_{m1(1)} + \Sigma A_{m2(1)}} \right) \left( \frac{\Sigma A_{m1(2)}}{\Sigma A_{m1(1)} + \Sigma A_{m2(1)}} \right),
\]

FIG. 3. Comparison of the predicted optima (---) and critical blocking concentration (-----) for hard spheres with measured optimum dosages at (C) \(1 \times 10^{-5}\), (T) \(1 \times 10^{-4}\), and (C) \(1 \times 10^{-5}\) mol L\(^{-1}\) KNO\(_3\).
A plot of Eq. (20) as a function of particle size ratio from this expression is presented in Fig. 4 for a range of $D_{11}$ values. It is evident from this plot that as $D_{11}$ increases, the number of small particles required to achieve large-large blocking increases such that their lateral separation on the large particle surface is decreased. Thus, as expected from the aggregation rate measurements, the optimum dosage for lower particle size ratios should increase with decreasing electrolyte concentration, opposite to the trend predicted and observed for similarly sized particles.

An interesting point to note with regard to the measured data for $R_2/R_1 = 0.36$ shown in Table II is that, from the above analysis, the decrease followed by an increase in optimum dosage with decreasing electrolyte concentration indicates a crossover to the large-large blocking regime for optimum dosage. For any given size ratio, at a sufficiently low electrolyte concentrations, this crossover should occur as the distance of closest approach becomes large relative to $R_2$.

Of course, for $D_{11}$ values in excess of the smaller particle diameter, it is impossible for a small particle to bridge the distance of closest approach of the large particles. At size ratios approaching $(D_{11}/2)$ the number of particles required for blocking approaches infinity. This is observed in Fig. 4 as the asymptotic approach of the concentration curves to the dotted lines indicating $R_2 = (D_{11}/2)$. An important point to remember though is that $D_{11}$ itself is a function of particle concentration such that as an increasing number of small particles are adsorbed to a larger particle surface, $D_{11}$ decreases. So, for a given size ratio, additional adsorbed particles reduce $D_{11}$ potentially allowing bridging to occur.

### C. Observations from literature

Further support for the proposed modification may be found in literature in the form of several observations made by other authors. Namely, these are an increasing asymmetry in dosage response curves with decreasing electrolyte concentration and the formation of chainlike aggregates at low electrolyte concentrations.

Dosage response data have been reported by Puertas et al. for the heteroaggregation of identically sized anionic and cationic PSL particles at different pH values. The pH was adjusted so as to vary the surface charge densities of the particles and therefore their surface potential. While a symmetric response curve centered on $(N_2/N_1)_{opt} = 1$ was reported for an equivalent surface charge density, asymmetry was observed for nonequivalent charge densities, maximum aggregation rate favoring an excess of the less charged particles. While the observations of Puertas et al. cannot be explained within the scope of the hard sphere model, inclusion of $D_{11}$ in the geometric derivations of collision provides clarification.

Assuming that the rate of decay of potential in the diffuse region of the double layer is independent of surface potential (that is, the exponent of decay remains the same, as predicted by the Debye-Hückel approximation), $D_{11}$, $D_{22}$, and $D_{12}$ must shorten with decreasing surface potential as they are proportional to the potential of double layer interaction. By summing the individual potentials at any given point from the two surfaces, a contour plot of the potential profile may be drawn (Fig. 5). The assumption that overlapping potentials are additive, the superposition approximation is strictly only applicable at large distances from the interacting surfaces (several Debye lengths). Consequently, the contours in Fig. 5 have not been extended beyond twice the Debye length. Rather than a symmetric potential distribution surrounding the two equivalent sized particles, as would be expected for equivalent surface potential, an asymmetric pattern is seen.

The asymmetric potential distribution pattern seen in Fig. 5 and the resulting differences in $D_{11}$, $D_{22}$, and $D_{12}$ imply that the effective collision areas for the two different particles are nonequivalent ($SA_{1(1)} \neq SA_{2(2)}$ and $SA_{1(2)} \neq SA_{2(1)}$). Optimization of Eq. (2) for maximum collision in such a situation indicates that a greater number of the less charged particle species are required, as observed by Puertas et al. In a physical sense, additional particles are required in order to equate the effective collision area of each particle species thus maximizing the effective surface heterogeneity of the system. At high electrolyte concentrations it is likely that the asymmetry of the response curve is lessened such that as the double layer thickness approaches zero the response curve regains complete symmetry.

Another interesting observation from the literature is the
optical micrograph presented by Kim et al.\textsuperscript{12} which shows chainlike heteroaggregates formed in de-ionized water, reportedly reaching up to 20 particles in length before branching occurs (a particle adsorbed to three other particles rather than two). This lack of branching was found to be preserved within the structure of larger aggregates for which micrographs were also obtained. From the perspective of the geometric collision efficiency model presented previously\textsuperscript{2} with the modification made in this work, the existence of chainlike aggregates of varying lengths can be explained in terms of a statistical probability. Since the area available for collision with an end particle is greater than that for a central particle, the chance of collision with an end particle is greater provided the number of central particles is low. As the chain length increases, the number of central particles increases, reducing the chance of collision with an end particle.

With decreased screening of particle surface charge the potential distribution pattern around a straight chain aggregate expands outwards. Approximating a particle chain as a cylinder with hemispherical ends, as the radius of the cylinder (and hemispheres) increases, the surface area of the hemispheres increases at a greater rate than that of the sides of the cylinder. Thus the chance of collision with an end particle increases as the Debye length increases. So we expect that while only short chains will be observed in high electrolyte concentrations, the average length of these chains will increase as the electrolyte concentration is decreased, thus accounting for the observations of Kim et al.

V. SUMMARY

A previously proposed model for the collision efficiency factor\textsuperscript{2} of clusters of hard spheres has been extended to allow for repulsive and attractive particle interactions to occur at some distances from the surface of particles (the distances of closest approach and furthest attraction for repulsive and attractive interactions, respectively). Expressions for the area of particles exposed to collisions were derived taking these distances into consideration.

While quantitative predictions are not possible using the extended model since the distances of closest approach and furthest attraction cannot be determined, some qualitative trends were observed with regard to optimum dosage. For similar sized particles, those for which the optimum dosage is unaffected by the blocking of large-large interactions, a decrease in optimum dosage with increasing double layer thickness (interaction distance) was observed. This may be understood in terms of an increasing interaction distance negating any finite difference in size between particles such that the effective collision area of each is the same for an infinite interaction distance. Conversely, for dissimilar sized particles, for which the optimum dosage is dictated by the blocking of large-large interactions, an increase in optimum dosage was observed with increasing double layer thickness. This observation was explained in terms of the increase in number of particles required to block such interactions at nonzero separation.

Several observations from literature were also explained in terms of the modified geometric collision efficiency model presented. These were the asymmetric dosage response curves observed by Puertas et al.\textsuperscript{3,4} and the increase in length of chainlike aggregates with decreasing electrolyte concentration observed by Kim et al.\textsuperscript{12} Both literary observations were explained in terms of the effect of varying interaction distances on the effective collision area of particles.

ACKNOWLEDGMENTS

The authors acknowledge the support of the Centre for Multiphase Processes, a Special Research Centre of the Australian Research Council. One of the authors (A.O.) also acknowledges the support of the School of Environmental and Life Sciences at the University of Newcastle.

APPENDIX: DERIVATION OF CRITICAL BLOCKING CONCENTRATION

Assuming an even distribution of small particles across the larger particle surface in a hexagonal configuration, the center of each small particle is situated at the vertex of up to six equilateral triangular planes or “faces.” The number of triangular faces created is given by...
\[ n_f = 2 \left( \frac{N_2}{N_1} - 2 \right). \]  
(A1)

The surface area of the larger particle underlying each face is then simply the total surface area of the particle divided by the number of faces, which may be expressed as

\[ \Delta = 2\pi R_1^2 \left( \frac{N_1}{N_2 - 2N_1} \right). \]  
(A2)

For most values of \( N_2/N_1 \), there will not be an integral number of equivalent triangular faces formed; however, this assumption should serve as a reasonable approximation. The underlying area of particle surface for each face is a spherical triangle, with all sides and angles being equal. The area of each spherical triangle is given by Girard’s theorem,

\[ \Delta = R_1^2 (3\alpha - \pi). \]  
(A3)

Equating Eqs. (A2) and (A3), the dihedral angle (\( \alpha \)) of each spherical triangle, the angle between the planes passing through the vertices of the triangle and the center of the inner sphere, is given by

\[ \alpha = \frac{N_2\pi}{3(N_2 - 2N_1)}, \]  
(A4)

where \( \alpha \) is expressed in radians. From the dihedral angle, the mean angle of separation between particles, with respect to the center of the inner sphere, can be calculated using the spherical trigonometry analog of the law of cosines,

\[
\phi = \cos^{-1}\left( \frac{\cos \alpha}{1 - \cos \alpha} \right). \tag{A5}
\]

Referring to Fig. 6, the distance of separation between two large particles at the critical blocking concentration is equal to the distance of closest approach of these particles \( (D_{11}) \). The distance from the midpoint between the two larger particles along their central axis to the center of a small particle is given by Pythagoras’ theorem,

\[
c_{b(\text{min})} = \sqrt{R_2(2R_1 + R_2) - D_{11} \left( R_1 + \frac{D_{11}}{4} \right)} \tag{A6}
\]

The linear separation between adjacent small particles \( l_{b(\text{min})} \) is then given by

\[
l_{b(\text{min})} = \sqrt{3R_2(2R_1 + R_2) - 3D_{11} \left( R_1 + \frac{D_{11}}{4} \right)} \frac{1}{\sqrt{2}}, \tag{A7}
\]

since \( l_b = \sqrt{3}c \). Applying the law of cosines to the triangle formed by joining the centers of two adjacent small particles and the large particle,

\[
\cos \phi_{b(\text{min})} = 1 - \frac{3R_2(2R_1 + R_2) - D_{11}(R_1 + D_{11}/4)}{2(R_1 + R_2)^2}, \tag{A8}
\]

which, by taking the inverse cosine, yields the required angle of separation between small particles adsorbed to the surface of the larger particle to block large-large interactions at the distance of closest approach of large particles, \( D_{11} \). Equating Eq. (A8) with the cosine of Eq. (A5), the number of evenly distributed small particles required to block interactions between large particles at a distance \( D_{11} \) is given by the expression

\[
\frac{N_2}{N_1} = 2 - 4\pi \left[ 6 \sin^{-1} \left( \frac{3D_{11}(D_{11} + 4R_1) + 4(2R_1^2 - 2R_1R_2 - R_2^2)}{3D_{11}(4R_1) + 4(4R_1^2 + 2R_1R_2 + R_2^2)} \right) - \pi \right]^{-1}. \tag{A9}
\]

which reduces to

\[
\frac{N_2}{N_1} = 2 - 4\pi \left[ 6 \sin^{-1} \left( \frac{2R_1^2 - 2R_1R_2 - R_2^2}{4R_1^2 + 2R_1R_2 + R_2^2} \right) - \pi \right]^{-1} \tag{A10}
\]

for hard spheres \( (D_{11}=0) \).