Theoretical study of orientation effects during the multi-particle diffuse double layer interaction in monodisperse aqueous zinc oxide nanocolloids

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Abstract

The work presents a theoretical study of the colloid nanoparticle agglomeration with a focus on the morphology of the resulting assemblages. This is achieved by using an original analytical multi-particle interaction model. It has been shown that the electrosteric repulsion between colloid nanoparticles makes it more energetically favourable to form linear structures; this effect is stronger for particles with higher surface charge. Linear agglomerates, however, turn out to be unstable and subjected to deagglomeration or compaction due to the surface-bound brownian motion of the constituent particles. Therefore the resulting morphology of a nano-agglomerate can be described as the product of a balance between the initial preference for a linear structure formation and further compaction or deagglomeration.

1 Introduction

Nanotechnology is among the fastest growing fields of applied research in the past few decades. An important group of nanomaterials that have found a wide industrial, commercial and scientific application are those based on nanoparticles as their primary structural units. These materials include nanocolloids, aerosols, nanoceramics, etc. and demonstrate a high dependency of bulk material properties on those of the individual nanoparticles [1].

It is important to note that physical and chemical properties of particle-based materials and, therefore, their fate and transport, biological activity and behaviour in the human body are also dependent on the morphology and stability of the particle assemblages [2, 3] in the form of agglomerates and aggregates (terms used in accordance with ISO 14887). Although the agglomeration of nanoparticles has been a subject of extensive studies, only a few works to date have focused their attention on the formation of nano-agglomerate spatial structure [2].

The present work is devoted to the theoretical study of nanoparticle agglomeration in aqueous colloids and is specifically focused on analysing the morphology of forming particle assemblages. Analytical description and analysis of nanoagglomerate structure is achieved by employing a modified version of the original multiparticle colloid interaction model first introduced by the authors in [5]. The model
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Figure 1: Schematic representation of a colloid ZnO nanoparticle’s charged surface and ionic atmosphere.

is developed in the framework of the DLVO (Derjaguin, Landau, Verwey, Overbeak) theory that assumes that interparticle interaction in colloid solutions is governed by two processes: short-range van der Waals attraction and long-range electroosmotic repulsion due to overlapping electric double-layers (EDL).

2 Methods

2.1 Mathematical model

We consider a spherical nanoparticle suspended in electrolyte solution as a spherically symmetric system with radial coordinate \( r \) (see figure 1). The colloid particle obtains surface charge through the processes of adsorption and desorption, which will be discussed in detail later. Thus we assume that the particle and the adsorption layer can be represented as a sphere of the effective radius \( a \) and uniform surface charge \( \sigma \). The charged particle is then subjected to solvation and thus acquires a charge-less hydration shell of roughly two water molecule diameters thickness \( \delta \) [7]. The layer of polarized \( \text{H}_2\text{O} \) molecules \( a < r < b = a + \delta \) (see figure 1) is known
to have significantly smaller effective dielectric permittivity in comparison with the bulk water [7]. The hydrated nanoparticle is surrounded by a diffuse ion atmosphere \( r > b \) that compensates the particle surface charge. To describe the discussed EDL structure we therefore have to consider two calculation domains:

\[
\begin{align*}
&I : \ a < r < b, \quad \epsilon_I = \epsilon_h \\
&II : r > b, \quad \epsilon_{II} = \epsilon
\end{align*}
\]

where the domains I and II correspond to the charge-less gap with the effective dielectric permittivity \( \epsilon_h \) and the diffuse layer with the bulk dielectric permittivity \( \epsilon \) respectively. The electric potential distribution \( \phi(r) \) in these domains is described by the following Debye-Huckel equation system:

\[
\begin{align*}
&\Delta \phi_I = 0, \quad a < r < b \\
&\Delta \phi_{II} = \kappa^2 \phi_{II}, \quad r > b
\end{align*}
\]

with boundary conditions:

\[
\frac{d}{dr} \phi_I|_{r=a} = -\frac{\sigma}{\epsilon_h \epsilon_0} \\
\phi_I(b) = \phi_{II}(b) = \phi_0 \\
\epsilon_h \frac{d}{dr} \phi_I|_{r=b} = \epsilon \frac{d}{dr} \phi_{II}|_{r=b} \\
\phi_{II}|_{r=-\infty} = 0
\]

Here \( \kappa \) is the reciprocal of the Debye length:

\[
\kappa = \left( \frac{2I}{\epsilon \epsilon_0 kT} \right)^\frac{1}{2}
\]

where \( I = \sum_i (z_i)^2 n_i \) - the ionic strength of the solution; \( i \) - number of the dissociated solute; \( z_i \) - charge number of the ions resulting from the dissociation of the \( i \)-th solute; \( e \) - elementary charge; \( \epsilon_0 \) - dielectric constant; \( k \) - Boltzmann constant; \( T \) - temperature.

Solving (2) with (3) for the diffuse layer we obtain:

\[
\phi_{II}(r) = \phi_0 \cdot \frac{b}{r} \cdot \exp \left[ -\kappa (r - b) \right]
\]

where \( \phi_0 \) is the zeta-potential:

\[
\phi_0 = \frac{1}{4\pi \epsilon_0 \epsilon} \frac{4\pi a^2 \cdot \sigma}{b(1 + \kappa b)}
\]

The nanoparticle obtains its surface charge through adsorption and desorption. For amphoteric particles such as ZnO the dominant charging process is competitive protonation and deprotonation of surface \(-\text{OH}\) groups [4, 7], which is demonstrated in figure 1. The corresponding reactions are:

\[
-\text{OH} + \text{H}^+ \rightleftharpoons -\text{OH}_2^+ \\
-\text{OH} + \text{OH}^- \rightleftharpoons -\text{O}^- + \text{H}_2\text{O}
\]
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We assume that all ions in the system except for the $\text{H}^+$ and $\text{OH}^-$ are indifferent to the particle surface. Linearisation of the potential-dependent $\text{H}^+$ and $\text{OH}^-$ concentrations at the particle surface in the non-saturated adsorption limit yields a simple expression for the surface charge density $\sigma$ of a nanoparticle placed in an external electric field:

$$\sigma = \sigma_0 + e \left[ \beta_+ n_{\text{H}} \left( 1 - \frac{e \varphi}{kT} \right) - \beta_- n_{\text{OH}} \left( 1 + \frac{e \varphi}{kT} \right) \right] \frac{1}{1 + \frac{e^2 (\beta_+ n_{\text{H}} + \beta_- n_{\text{OH}})}{4\pi \varepsilon \varepsilon_0 kT} \left[ \frac{1}{b(1+kb)} + \frac{b-a}{ab} \right]}$$

where $\sigma_0$ - constant portion of the surface charge density due to charged groups that are not involved in any chemical reactions in the considered system; $n_{\text{H}}, n_{\text{OH}}$ - bulk $\text{H}^+$ and $\text{OH}^-$ concentrations in the solution; $\varphi$ - local potential of the external electric field; $\beta_+, \beta_-$ - model fitting parameters.

Using (6) and the non-saturated charge regulation model (8) we can obtain the expression for the zeta-potential dependency on $\text{pH}$ and use for the experimental data fitting and thus obtain the numerical values for the model parameters $\beta_+, \beta_-$ (see figure 2). The suggested theoretical approach is suitable for the spherical amphoteric nanoparticles with low surface potential suspended in the aqueous solutions of low ionic strength. Therefore, the zinc oxide nanoparticles were chosen for the modelled system of this work due to their unique semiconductor and chemical properties wide use in customer products.

Using the monopole approximation, we substitute each particle with its equivalent screened point-charge [8] :

$$Q = 4\pi \varepsilon \varepsilon_0 \cdot \varphi_0 \cdot be^{kb}$$

Figure 2: Comparison of the ZnO nanoparticle zeta-potential dependency on pH obtained using the proposed non-saturated charge regulation model (solid line) with the experimental data from [6] (dots). The dashed vertical lines mark the limits of applicability of the model.
Then the potential energy of a particle number $\alpha$ interacting with multiple other particles can be found as:

$$U_{\alpha}([R_{\alpha,\beta}]) = \frac{Q_{\alpha}}{4\pi\varepsilon_0} \cdot \sum_{\beta \neq \alpha} Q_{\beta} \cdot \frac{\exp\left(-\kappa R_{\alpha,\beta}\right)}{R_{\alpha,\beta}} + \sum_{\beta \neq \alpha} [U_{vdW}(R_{\alpha,\beta})]$$

(10)

where $\alpha$, $\beta$ - particle numbers; $R_{\alpha,\beta}$ - centre-to-centre separation between particles $\alpha$ and $\beta$; the equivalent charges $Q_{\alpha}$ can be found from the linear algebraic equation system:

$$Q_{\alpha} + \sum_{\beta \neq \alpha} \theta_{\alpha,\beta} \cdot Q_{\beta} = Q_{ISO}$$

(11)

here $Q_{ISO}$ - the equivalent charge of an isolated particle; the matrix coefficients are:

$$\theta_{\alpha,\beta} = \frac{1}{4\pi\varepsilon_0} \cdot \frac{e^2}{kT} \cdot \frac{1}{R_{\alpha,\beta}(1 + k\beta)} \cdot \frac{(\beta_H n_H + \beta_{-OH} n_{-OH}) \cdot \exp\left[-\kappa (R_{\alpha,\beta} - b)\right]}{1 + \frac{e^2[\beta_H n_H + \beta_{-OH} n_{-OH}]}{4\pi\varepsilon_0 kT} \left[\frac{1}{b(1+k\beta)} + \frac{b-a}{ab}\right]}$$

(12)

The van der Waals attraction energy in (10) is given by [7]:

$$U_{vdW}(R) = -\frac{A}{6} \left[\frac{2a^2}{R^2 - 4a^2} + \frac{2a^2}{R^2} + \ln\left(\frac{R^2 - 4a^2}{R^2}\right)\right]$$

(13)

where $A$ - the effective Hamaker constant for the particle interaction through an intervening medium.

Thus we have obtained the expression (10) for the multi-particle colloid interaction potential energy for arbitrary particle positions using the non-saturated charge regulation model (8).

### 2.2 Model validation

The derived expression for the inter-particle interaction energy allows us to study the potential barrier arising when a nanoparticle is approaching a certain agglomerate configuration. Assuming that the nanoparticle velocity distribution during its Brownian motion approaches the Maxwellian one for times much longer than the duration of a single molecule collision [9], we can calculate the probability of nanoparticle possessing enough kinetic energy overcome the given potential barrier. The corresponding probability function for the particle having the kinetic energy $E$ greater than the potential barrier energy $E_b$ is depicted on figure 3.

For the case of a nanoparticle approaching an agglomerate the proposed model predicts a limited growth of the potential barrier with the increase of the agglomerate’s size. After a certain agglomerate size the potential barrier for attachment reaches a plateau and ceases to grow due to the charge redistribution between the particles. The corresponding attachment probability dependency on the agglomerate size is illustrated on figure 4. As shown in the figure, the traditional linear superposition approximation [8] that does not account for the charge regulation predicts the termination of agglomeration for assemblages of more than 13 particles, which significantly contradicts the experiment data (see the inset on figure 4) [6].
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Figure 3: Probability of nanoparticle having the kinetic energy \( E \) greater than the potential barrier energy as a function of its value \( E_b \).

On the contrary, the proposed model predicts a limited decrease of the attachment probability reaching a constant high value for the agglomerates of more than 13 constituent particles demonstrating a good qualitative agreement with the experiment.

Figure 4: Probability of nanoparticle attachment to an agglomerate as a function of the agglomerate’s size (expressed as a number of constituents particles) obtained with and without the charge regulation model for pH = 7.7; the inset illustrates the experimental pH dependency of the mean agglomerate size taken from [6].

3 Results and discussion

The presented multi-particle interaction model was used to study the attachment of a nanoparticle to a certain set of 2-, 3-, 4- and 5-particle agglomerate configurations.
Figure 5: Contour plots of the interaction potential energy between a single mobile nanoparticle and a fixed agglomerate configuration; brighter areas correspond to higher values of the potential energy. The nanoparticle is moving in a plane with a selected orientation relative to the agglomerate. The considered agglomerate configurations are: a) 2-particle agglomerate; b) compact 3-particle agglomerate; c) linear 3-particle agglomerate; d) compact 4-particle agglomerate; e) linear 4-particle agglomerate; f) compact 5-particle agglomerate; g) linear 5-particle agglomerate.

To analyse the possible resulting agglomerate morphologies and identify the most energetically favourable of them we have studied the dependency of the interaction potential energy on the location of nanoparticle attachment site on the agglomerate. The resulting potential energy contour plots for the selected agglomerate orientations are depicted in figure 5. The figure shows that the potential barrier due to electroosmotic repulsion is anisotropic with respect to the direction of particle’s approach: attachment to a site with more particles in contact results in higher barrier.

The observed electroosmotic orientation effects during agglomeration are further illustrated in figure 6 which demonstrates the dependency of the attachment probability on the direction of the nanoparticle approach for different solution pH values. According to figure 2 pH values that are further away from the neutral pH result in higher particle surface charge and, therefore, the increasing role of electroosmotic repulsion in particle interactions. This explains the corresponding increase of the attachment probability anisotropy for the approach directions found in figure 6.

It is thus shown that with the increase of the nanoparticle surface charge it becomes more and more energetically favourable to initially form linear structures. Figure 6 also shows that for linear agglomerates the attachment of each next particle in a continuation of the linear structure becomes more and more plausible.

The fate of the agglomerate after its initial formation is studied in figure 7. This figure depicts the dependency of the potential well depth on the attachment
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Figure 6: Probability of a nanoparticle attaching to an agglomerate of a specific morphology as a function of the particle’s approach direction. The nanoparticle is moving in a plane with a selected orientation relative to the agglomerate. The considered agglomerate configurations are: a) 2-particle agglomerate; b) compact 3-particle agglomerate; c) linear 3-particle agglomerate; d) compact 4-particle agglomerate; e) linear 4-particle agglomerate; f) compact 5-particle agglomerate; g) linear 5-particle agglomerate.

- Radial coordinate - attachment probability at:
  - neutral pH
  - pH = 7.75
  - pH = 7.9

- Angular coordinate - direction of particle’s approach
  - schematic agglomerate representation

Figure 7: Depths of the potential well corresponding to different attachment sites. Namely, the most energetically favourable from the long-range electroosmotic repulsion point of view sites in contact with only one particle are associated with the potential well of $3kT$. According to figure 3 a particle can escape such a well due to solvent molecules collisions. Potential wells for the sites in contact with two and more particles are deep enough to be considered a permanent attachment.

Therefore, attachment sites with a single particle in contact, which were shown as the most energetically favourable from the electroosmotic repulsion point of view, are unstable due to the surface-bound brownian motion of the attached nanoparticle. The said chaotic motion can either cause the detachment of the particle, or position it near one of the more favourable van der Waals sites and cause the agglomerate compaction.

As a result, according to the proposed model the predominant type of agglomer-
Figure 7: Potential well depth for the nanoparticle attached to the agglomerate of a specific morphology as a function of the attachment site position. The attachment sites lying in a plane with a selected orientation relative to the agglomerate are considered. The agglomerate configurations are: a) 2-particle agglomerate; b) compact 3-particle agglomerate; c) linear 3-particle agglomerate; d) compact 4-particle agglomerate; e) linear 4-particle agglomerate; f) compact 5-particle agglomerate; g) linear 5-particle agglomerate.

erates in the system with high nanoparticle surface charge will be determined by the balance between the initial linear structure formation and their further gradual deagglomeration or compaction due to the surface-bound brownian motion of the constituent particles and the close-range van der Waals repulsion. The model also predicts the decrease of linear agglomerate fraction in the systems with smaller particle surface charges.

References


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