Theoretical study of the morphology of self-assembled amphoteric oxide colloid nanocrystals in weak electrolyte solutions

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Abstract. The present paper is devoted to the theoretical study of the morphology of nanocrystals formed through self-assembly of amphoteric oxide colloidal nanoparticles in weak electrolytes. A mathematical model of multi-particle colloidal interaction was developed within the framework of the Derjaguin, Landau, Verwey, Overbeak (DLVO) theory. This model accounts for the surface charge regulation during the multi-particle interaction and reveals the presence of orientation effects during nanoparticle aggregation. These effects are presumed to affect the morphology of the self-assembled nanocrystals and may present the means of controlling the structure of synthesised nanomaterials.

1. Introduction
Nanocrystalline materials are widely used in photonics and optoelectronics due to their unique properties. These properties include optical and electronic size effects, surface plasmon resonances, formation of photonic bandgaps in ordered structures, etc [1-5]. The specific parameters of synthesized nanocrystalline materials are strongly dependent on the morphology of their structural units – single nanocrystals or their assemblages [3-5]. Thus the creation of nanocrystalline materials with desired properties relies on the ability to produce the structural units of prescribed morphology. For example, manufacturing of highly efficient nanocomposite hybrid organic-inorganic solar cells requires the synthesis of three-dimensional hyperbranched colloidal semiconductor nanocrystals of specified dimensions [4].

Self-assembly in colloid systems is among the most cost-efficient and promising methods for obtaining nanocrystalline materials with specific structure [5]. One way of implementing this technique is through the controlled coagulation of colloid nanoparticles. This allows for using the colloid self-assembly to create nanoparticle assemblages with required morphology. The obtained nanoagglomerates can be then employed for the synthesis of a variety of nanocomposite materials and photonics glasses [5].

The present paper is devoted to the theoretical study of amphoteric oxide nanoparticles’ self-assembly in aqueous solutions of weak electrolytes. An original mathematical model is used to explore the effect of the colloidal system parameters on the morphology of the self-assembled agglomerates.

2. Methods
Theoretical study of the colloidal self-assembly of nanoparticles is carried out using an original colloidal multi-particle interaction model introduced by the authors in [6, 7]. The model was developed in the framework of the Derjaguin, Landau, Verwey, Overbeak (DLVO) theory. This theory assumes that the interaction between colloid particles can be represented using the attractive van der
Waals term and the repulsive electroosmotic term. The latter arises due to the overlap of particles’ electric double layers (EDLs).

The developed colloidal interaction model uses an original nanoparticle surface charge regulation model along with the representation of the electric potential distribution in nanoparticle’s EDL through the first few terms of its multipole expansion to solve the Debye-Hückel equation for the system of multiple interacting particles, as described by the authors in [7].

In the present work we limit ourselves to the simple case of using the monopole approximation for the potential distribution in the EDL of a colloidal particle. In this case, the developed charge regulation model yields the following expression for the nanoparticle’s surface charge density \( \sigma \):

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

where \( \sigma_0 \) - constant portion of charge; \( n_{\text{H}^+}, n_{\text{OH}^-} \) - bulk \( \text{H}^+ \) and \( \text{OH}^- \) concentrations; \( a, b \) - physical and hydrodynamic particle radii; \( \beta_n, \beta_n \) - coefficients proportional to the sums of the rate constants for the adsorption processes involved; \( \phi \) - potential of the external field; \( e \) - elementary charge. The model parameters \( \sigma_0 \) and \( \beta_n, \beta_n \) were calculated using the experimental zeta-potential dependency on pH taken from [8].

As it has been shown in [7] by the authors, the potential energy \( U_\alpha \) of a colloidal nanoparticle interacting with multiple other particles in the considered system can be found as:

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

where \( \alpha, \beta \) - particle numbers; \( R_{\alpha,\beta} \) - centre-to-centre separation between particles \( \alpha \) and \( \beta \); \( \varepsilon \) - effective dielectric permittivity in the diffuse ion layer; \( \varepsilon_0 \) - dielectric constant; \( \kappa \) - reciprocal of the Debye screening length; \( U_{\text{vdW}} \) - potential energy of van der Waals attraction; \( Q_\alpha \) - equivalent screened point-charge of the particles \( \alpha \) that can be than found by solving the following linear system of algebraic equations:

\[
Q_\alpha + \sum_{\beta \neq \alpha} \theta_{\alpha,\beta} \cdot Q_\beta = Q_0
\]

with the coefficient given by:

\[
\theta_{\alpha,\beta} = \left( 1 + e^2 \left[ \beta_n n_{\text{H}^+} + \beta_n n_{\text{OH}^-} \right] \frac{1}{4 \pi \varepsilon_0 kT \left[ b(1 + kb) + \frac{b-a}{ab} \right]} \right) \frac{1}{\frac{\beta_n n_{\text{H}^+} + \beta_n n_{\text{OH}^-}}{b(1 + kb) + \frac{b-a}{ab}}}
\]

\( Q_0 \) - equivalent charge of an isolated particle.

The model validation was performed by studying its predictions for the dependency of the probability of a nanoparticle attaching to an agglomerate on the agglomerate’s size. The developed model provides good qualitative agreement with experimental data for this dependency, as it has been shown in [7].

3. Results and discussion

The developed mathematical model of colloidal multi-particle interaction was used to study the morphology of self-assembled nanoparticle agglomerates. The case of a single nanoparticle attaching to an agglomerate of varied size was modelled. This allowed to explore the effects of the colloidal solution properties on the geometry of the agglomerates being formed.

Firstly, we have studied the dependency of the interaction potential energy on the location of the single nanoparticle in relation to the surface of the agglomerate. This allowed us to analyze the possible resulting agglomerate morphologies and identify the most energetically favourable of them.
The cases of a single nanoparticle approaching the agglomerate formed by 2, 3, 4 or 5 particles were considered.

The corresponding potential energy contour plots for the electroosmotic interaction potential energy are depicted in figure 1. 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 a higher potential barrier. It should be noted that figure 1 demonstrates two options for the geometry of 3-, 4- and 5-particle agglomerates. One option is the linear structure found to be most energetically favourable with regards to electroosmotic repulsion. The other option is the close-packed structure that is most energetically favourable with regards to van der Waals attractions.

![Figure 1](image)

**Figure 1.** Contour plots of the interaction potential energy between a single mobile nanoparticle and a fixed agglomerate configuration normalized to its maximum value; brighter areas correspond to higher values of the potential energy. 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.

The observed electroosmotic orientation effects during agglomeration are further illustrated in figure 2. This figure demonstrates the dependency of the attachment probability on the location of the attachment site on the surface of the agglomerate for different solution pH values. The attachment site position on the surface is given by its angular coordinate. 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 2.

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 2 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 3. This figure depicts the dependency of the potential well depth on the attachment site location on the surface of the agglomerate. The attachment site position on the surface is given by its angular coordinate.
Figure 2. 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.

Figure 3. 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.
According to figure 3 the depth of the potential well is maximum for the attachment sites that have as many as possible particles in close contact. It is important to note that the van der Waals potential wells corresponding to the most favourable attachment sites are highly localized. Away from these sites the attractive potential energy holds constant. This means that the van der Waals attraction will not give rise to the compacting force acting on the attached particle unless it is in a close proximity with the favourable site.

Figure 3 also shows important results that arise from the absolute values of the attraction potential wells’ depths. Namely, the sites in direct contact with only one particle of the agglomerate are associated with the potential well energy of $3kT$. Therefore, 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.

Thus, attachment sites with a single particle in contact, which were shown as the most energetically favourable with regards to the electroosmotic repulsion, 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 agglomerates 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.

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References
[1] Shipway A N et al 2000 ChemPhysChem 1 (1) 18
[2] Talapin D V et al 2010 Chem. Rev. 110 389
[3] Li W et al 2013 J. Am. Chem. Soc. 135 4664
[4] Gur I et al 2007 Nano Lett. 7 (2) 409
[5] Kim S-H et al 2011 NPG Asia Mater. 3 (1) 25
[6] Alfimov A V et al 2014 J. Phys.: Conf. Ser. 541 012063
[7] Alfimov A V et al 2015 Proceedings of SPIE 9519 951911
[8] Berg J M et al 2009 Nanotoxicology 3 (4) 276
[9] Ohshima H 1995 Journal of Colloid and Interface Science 174 (1) 45