An analytical method for determining the interaction energy between multiple identical spherical colloidal zinc oxide nanoparticles

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Abstract. A modification of the linear superposition approximation for the linearized Poisson-Boltzmann equation, describing the interaction of colloidal nanoparticles, is proposed based on the implementation of a phenomenological charge regulation model to allow for the more accurate description of the interaction at small particle separations and multi-particle interactions.

1. Introduction
The problem of analytical description of the interaction forces between colloidal nanoparticles is of a great importance for the modern science due to the wide variety of applications for nanocolloid-based materials and the problem of their toxicity [1 – 3].

The standard and well-established approach to describing the interaction between colloidal particles in electrolytes is the DLVO (Derjaguin, Landau, Verwey, and Overbeak) theory and various modifications and additions to it [1, 4]. The core of this interaction theory is the combination of short-range van der Waals attraction and long-range electrosteric repulsion due to the overlap of particles’ electric double-layers (EDL). The spatial potential distribution in the EDLs of isolated and interacting particles is governed by the Poisson-Boltzmann equation, which is the Poisson equation with the volume charge density represented by the concentrations of positively and negatively charged ions obeying the Boltzmann distribution.

In the case of low surface potential \( \varphi_0 \) of particles: \( \varphi_0 \ll kT/e \), where \( k \) - Boltzmann constant; \( T \) - temperature; \( e \) - elementary charge, the Poisson-Boltzmann equation allows for linearization and takes the form of:

\[
\Delta \varphi = \kappa^2 \varphi ,
\]

where \( \kappa = \lambda_D^{-1} \) - inverse Debye screening length which for the simplest case of particles suspended in distilled water is given by \( \kappa = (2e^2 n_0/\varepsilon \varepsilon_0 kT)^{1/2} \), \( n_0 \) - concentration of H\(^+\) and OH\(^-\) ions at an infinite separation from suspended particles.

The applicability of existing methods for solving the Poisson-Boltzmann problem (1) for the system under consideration is determined by the order of magnitude of the expression \( \kappa a \), where \( a \) is a particle radius. For the case of \( \kappa a \ll 1 \), which generally describes nanoparticle suspensions in weak
electrolytes, the most well-studied method of Derjaguin’s approximation and its modifications are not applicable. Thus the leading approach to the Poisson-Boltzmann equation for interacting nanoparticles when $ka \ll 1$ is the linear superposition approximation (LSA), which suggests that the potential distribution in a system of multiple interacting particles can be presented as a sum of individual potentials of each particle involved when isolated from the others. Two main formulations of the LSA exist: the one by Bell, McCartney and Levine [5] and the one described by Ohshima [6].

Although the linearized equation (1) itself allows for the solution in a form of linear superposition of potential distributions due to each individual particle, the problem arises from the boundary conditions which are to be specified on the surfaces of every interacting particle. Thus the LSA is generally valid only at large separations between particles, when the disturbance of the surface potential of a particle by the proximity of another particle is negligible.

This paper presents a modified LSA approach (MLSA), where an effective single-particle potential distribution which reacts to the particle’s surroundings through a phenomenological charge regulation model is used to compensate for the boundary conditions violation by the conventional LSA.

2. Methods
We consider a spherical nanoparticle with radius $a$ and surface charge density $\sigma$ suspended in distilled water (see figure 1). The EDL of the particle is assumed to be composed of only two main layers: the dense Stern layer of counter-ions with the thickness of $\delta$ (zone I on figure 1) and the diffuse layer of co- and counter-ions (zone II on figure 1). We make an assumption that the counter-ion concentration is distributed uniformly in the Stern layer and equal to $N$.

The nanoparticle and its Stern counter-ion shell forms the effective particle with radius $b = a + \delta$. We further assume that the hydrodynamic radius of the particle equals to the effective particle’s radius $b$ and, thus, the potential on the surface of the Stern layer is equal to the $\zeta$-potential.

Spherical ZnO nanoparticles were chosen as the modeling objects for the present work as it has been shown [7] that they have sufficiently low surface potential in distilled water with neutral pH.

![Figure 1. Schematic representation of a colloid ZnO nanoparticle and its electric double layer: I – dense Stern layer of counter-ions; II – diffuse layer of co- and counter-ions.](image)

The Poisson-Boltzmann equations describing the discussed system are:

\[
\begin{align*}
\Delta \phi_I &= \epsilon N \cdot (\varepsilon \varepsilon_0)^{-1} & a < r < b \\
\Delta \phi_B &= \kappa^2 \phi_B & r > b
\end{align*}
\]

with the boundary conditions:

\[
\begin{align*}
\frac{d}{dr} \phi_I \bigg|_{r=a} &= -\frac{\sigma}{\varepsilon \varepsilon_0}, & \frac{d}{dr} \phi_I \bigg|_{r=b} &= \frac{d}{dr} \phi_B \bigg|_{r=b} \\
\phi_I(b) &= \phi_B(b), & \phi_B \bigg|_{r=\infty} &= 0
\end{align*}
\]
where $r$ - radial component of the spherical coordinate system connected with the centre of the particle.

The solution of the system (2) in the diffuse layer area II is given by:

$$\phi_0(r) = \phi_0 \cdot \frac{b}{r} \cdot \exp[-\kappa(r-b)],$$

where $\phi_0$ - potential on the surface of the Stern layer ($\zeta$-potential):

$$\phi_0 = \frac{1}{4\pi\varepsilon_0} \cdot \frac{1}{b(1+k\beta)} \cdot \left( \sigma \cdot 4\pi a^2 - e \cdot \Omega \right),$$

and $\Omega = N \cdot (4/3)\pi \left(b^3 - a^3\right)$ - total quantity of counter-ions in the Stern layer.

Expression (5) needs the parameters describing charge distribution, $\sigma$ (surface charge density) and $\Omega$ (ion quantity in the Stern layer), determined. To do so we introduce a phenomenological model of charge regulation which establishes the connection between the ambient concentrations of ions in the vicinity of the particle and the electrical charges on the surface and in the Stern shell of the particle.

The proposed linear model of nanoparticle’s surface charge has the form of:

$$\sigma(h^+_0) = \sigma' + \sigma^* \cdot h^+_0,$$

where $\sigma'$ is a constant part of the surface charge due to the surface features of the nanoparticle; $\sigma^* \cdot h^+_0$ is the part of the surface charge due to the adsorption of potential determining ions; $h^+_0$ is the ambient concentration of co-ions in the vicinity of the particle.

The linear model of the counter-ion total quantity in the dense shell is given by:

$$\Omega(h^-_0) = \omega \cdot h^-_0,$$

where $h^-_0$ is the ambient concentration of counter-ions in the vicinity of the particle.

Thus we obtain an expression for the effective surface potential ($\zeta$-potential) of a nanoparticle that is dependent on the ambient ion concentrations:

$$\phi_0^{\text{eff}}(h^+_0, h^-_0) = \frac{1}{4\pi\varepsilon_0} \cdot \frac{1}{b(1+k\beta)} \cdot \left(4\pi a^2(\sigma' + \sigma^* \cdot h^+_0) - e \cdot \omega \cdot h^-_0 \right).$$

To find the three introduced charge regulation parameters, $\sigma'$, $\sigma^*$ and $\omega$, one can use the experimental data on the $\zeta$-potential of the particles at different values of pH. Determining the co- and counter-ion concentrations at three different pH values and substituting them into the expression (8) with the according $\zeta$-potential values will result in a system of 3 linear algebraic equations with 3 variables. It should be noted that to find the charge regulation parameters one must also know or make an assumption on the Stern layer thickness for the three employed experimental cases.

With the connection between nanoparticle’s surface potential and the ambient ion concentrations established, we now assume that under the linear superposition approximation the ion concentrations in the vicinity of a nanoparticle can be presented as a combination of the bulk concentrations of co- and counter-ions and the concentration perturbations due to the EDLs of the surrounding particles. Knowing that the ion concentrations in the EDLs of the surrounding particles are governed by the Boltzmann distribution an using the expression (8) and the $k\alpha \ll 1$ condition, we can derive an expression for the effective potential distribution of the nanoparticle under consideration:

$$\phi^{\text{eff}}(r) = F_i\left(\left\{R_{i,j}\right\}\right) \cdot \frac{\exp(-k\alpha r)}{r},$$

where $\left\{R_{i,j}\right\}$ is a set of the center-to-center separations $R_{i,j}$ between the particle under consideration $i$ and all the surrounding particles; the function $F_i$ is determined by the effective potential distributions due to the surrounding particles:

$$F_i\left(\left\{R_{i,j}\right\}\right) = F_{\text{iso}} - \eta \cdot \sum_{j \neq i} \phi^{\text{eff}}(R_{i,j}),$$

where $F_{\text{iso}}$ is the isotropic potential of the particle under consideration.
where the $F_i$ function value for the isolated particle $F_{ISO}$ is given by:

$$F_{ISO} = \frac{1}{4\pi \varepsilon_0} \left[ 4\pi a^2 (\sigma^+ + \sigma^- n_0) - eon_0 \right]$$  \hspace{1cm} (11)

and

$$\eta = \frac{en_0}{4\pi \varepsilon_0 kT} \left[ 4\pi a^2 \cdot \sigma^- - e\omega \right].$$  \hspace{1cm} (12)

Thus, combining the expressions (9) and (10), for a system of $m$ interacting particles with the set of center-to-center separations $\{R_{i,j}\}$ we obtain a system of $m$ linear algebraic equations with $m$ variables:

$$F_i + \eta \cdot \sum_j F_j \cdot \exp(-\kappa R_{i,j}) = F_{ISO}.$$  \hspace{1cm} (13)

Solving the system (13) will allow for the determining of the effective potential distributions of each interacting particle using (9).

To find the potential energy of the multi-particle interaction for the nanoparticle under consideration $i$ we use the Ohshima’s LSA formulation [6]:

$$U_i(\{R_{i,j}\}) = Q^\eta_i \cdot \sum_j \varphi^\eta_j(R_{i,j}),$$  \hspace{1cm} (14)

where $Q^\eta_i = 4\pi \varepsilon_0 \cdot F_i$ - effective screened point-charge that creates the same potential distribution as the particle $i$.

3. Results and discussion

To illustrate the presented MLSA method we consider the problem of three interacting nanoparticles.

Figure 2. Three-particle interaction: a) considered interaction geometries; b) interaction potential energy $U$ dependencies on the distance $R$ between particles given by the LSA and the MLSA (for three nanoparticle collision geometries: symmetrical, A and B). $Ek$ – mean square kinetic energy of nanoparticle’s Brownian motion; $d$ – particle’s diameter.
The solution to the system (13) for the case of three interacting nanoparticles has a form of:

\[ F_i = F_{iso} \cdot \left( \frac{\gamma_{i,j} + \gamma_{i,k} - \gamma_{j,k} - 1}{(\gamma_{i,j})^2 + (\gamma_{i,k})^2 + (\gamma_{j,k})^2 - 2\gamma_{i,j} \cdot \gamma_{i,k} \cdot \gamma_{j,k} - 1} \right) \]

(15)

where \( \gamma_{i,j} = \eta \cdot \exp(-\kappa R_{i,j}) / R_{i,j} \).

We then use the experimental data from [7] to calculate the charge regulation parameters. To illustrate the obtained result (15) and compare it with the predictions of the conventional LSA for the case of three interacting nanoparticles we choose three specific geometries of nanoparticles collision (see figure 2,a): the symmetrical collision when the separations between each particle are equal; the geometry where separation between two particles is maintained constant and the third particle approaches them in the direction perpendicular to the line connecting “paired” particles’ centers (collision geometry A on figure 2,a) and the geometry where the third particle approaches “paired particles” in the direction parallel to the line connecting their centers (collision geometry B on figure 2,a).

**Figure 3.** a, b) Attachment probability \( \beta \) dependencies on the particle diameter \( d \) for 2, 3 and 4 interacting nanoparticles obtained using the LSA (a) and the MLSA (b) methods. c, d) Attachment probability \( \beta \) dependencies on the temperature \( T \) for 2, 3 and 4 interacting nanoparticles obtained using the LSA (c) and the MLSA (d) methods. The symmetrical collision geometry was used for the multi-particle cases.
Curves showing the dependences of the nanoparticles’ interaction potential on the separation between the particles obtained using the MLSA method for the three collision geometries discussed above are presented on the figure 2,a in thick lines. The interaction potential for three nanoparticles derived using the conventional LSA is also displayed on the figure 2,a in solid thin line; the pair interaction potential curve is also presented as a reference (thin dashed line on figure 2,a).

The potential curves presented on the figure 2 show that the increase in the potential barrier energy for the three-particle interaction in comparison with the pair interaction is sufficiently lower for the presented MLSA method than the results of the standard LSA model. This indicates that the MLSA model can overcome the problem of almost linear dependency of the barrier energy on the number of interacting particles observed in LSA. The differences between considered collision geometries also demonstrate the MLSA’s ability to describe some of the orientation effects during nanocluster formation.

Assuming that the kinetic energy of nanoparticle’s Brownian motion is distributed according to the Gaussian law with the mean square of $3kT/2$ ($kT/2$ per orthogonal direction), we can calculate the probability $\beta$ of a nanoparticle acquiring the kinetic energy of motion towards the other particles sufficient to overcome the potential barrier. This probability has a meaning of an attachment probability. It is important to notice that due to the way the attachment probability $\beta$ was introduced its maximum value equals to 0.5 as there is a 50% chance that the nanoparticle will move away from the other particles due to the random collisions with water molecules.

The dependencies of the attachment probability on the model parameters, i.e. nanoparticle size and temperature, obtained using the LSA and the MLSA for 2, 3 and 4 interacting particles are shown on figure 3. The symmetrical collision geometry was used for the multi-particle interactions. The figure shows that the MLSA generally results in smaller drop in attachment probability when considering more interacting particles when comparing it to the LSA results. Both models have good qualitative agreement with the experimental attachment probability dependancies on the temperature (see, for example, [8]).

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