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Analytical solution of the Poisson–Boltzmann problem for two-layer spherical cell model

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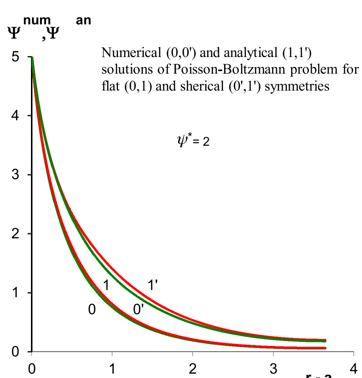
HIGHLIGHTS

- A two-layer cell model for solution of the Poisson–Boltzmann equation is proposed.
- The general solution can be obtained by matching of solutions in each of the layers.
- Correct choice of matching conditions provides high accuracy of a general solution.
- The model can be used for highly charged particles and arbitrary volume fraction.
- The type of particle packing strongly affects the potential distribution.

GRAPHICAL ABSTRACT



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ABSTRACT

The two-layer spherical cell model to describe the equilibrium electrical potential distribution between strongly charged particles in a monodisperse system is proposed. It is shown that the general solution of the Poisson–Boltzmann equation can be obtained by a combination of its solutions in the approximation of the excluded co-ions for the inner layer and in the Debye approximation for the outer one. The equation for the coordinate of the matching of solutions is proposed and analytically solved. It is shown that the correct choice of conditions for the matching provides a high precision of the solution in each layer. The article also analyzes the dependence of the characteristics of dispersed systems on the type of particle arrangement.

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1. Introduction

Since the early studies of the conductivity and dielectric permittivity of heterogeneous media [1] and hydrodynamic flows [2–4], the spherical cell model is widely used to describe a variety of equilibrium [5–8] and non-equilibrium [9–12] characteristics of disperse systems, in particular the sedimentation current and potential [13–15], electrophoretic mobility [16–19], electrical conductivity [17,20], dielectric dispersion [21], acoustic and electroacoustic properties [22], etc.

The cell model can be relatively easily applied to disperse systems either with a low surface potential and weak overlap of double layers (small volume fraction of particles) or with a high surface potential and a strong overlap of double layers (large volume fraction of the particles). In particular, in the case of highly charged spherical particles in concentrated disperse systems, the problem was analytically solved in the approximation of excluded co-ions [7]. However, the attempt to obtain an analytical solution of the

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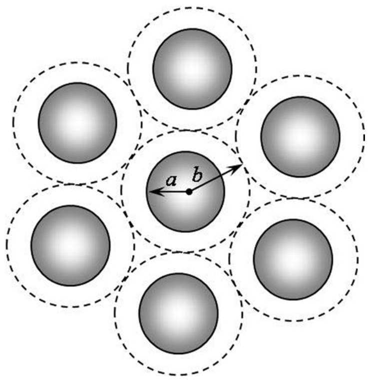

Fig. 1. Scheme of particles and layers in the one-layer spherical cell model.

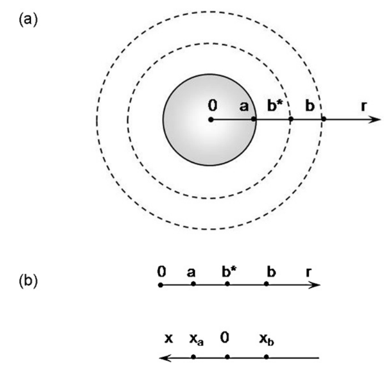

Fig. 2. (a) Scheme of a two-layer spherical cell model. (b) Scheme of transition from the old system of coordinates (r) to the new one (x).

Poisson–Boltzmann equation for disperse systems with arbitrary characteristics of an electric double layer and arbitrary volume fraction of particles causes a number of mathematical difficulties. Even the much simpler flat (one-dimensional) problem for high surface potentials at an arbitrary overlapping of electrical double layers was solved in a rather complicated way [23]. Thus, the lack of analytical solution of the Poisson–Boltzmann equation for the wide range of dispersion parameters significantly limits the theoretical analysis of disperse systems properties. Therefore, we have sought to find a solution of this problem which remained unsolved for many years.

This paper shows the analytical solution of the Poisson–Boltzmann equation for monodisperse systems consisting of highly charged spherical particles in uni-univalent electrolytes. The solution method is based on the well-known idea of the spherical cell model but, in contrast to the above-mentioned one-layer model, a two-layer spherical cell is introduced. Matching the solutions obtained for each of the layers, one can find a general solution for the electrical potential distribution between particles.

2. One-layer cell model at low surface potentials

The authors of conventional (one-layer) model present the disperse system as a set of identical spherical cells with particles in the center of each of them (Fig. 1). It is also supposed that the cell radius $\tilde{b}$ can be expressed through the volume fraction φ and the radius $\tilde{a}$ of particles as

$$\tilde{b} = \frac{\gamma \tilde{a}}{\sqrt[3]{\varphi}}, \tag{1}$$

where γ depends on the particle packing that will be discussed in Section 5.

First of all, let us obtain the analytical solution for weakly charged particles. Distribution of the potential in the continuous liquid phase satisfies the Poisson–Boltzmann equation, which in the case of spherical symmetry and uni-univalent electrolytes can be expressed in the dimensionless form as

$$\frac{d^2\psi(r)}{dr^2} + \frac{2}{r}\frac{d\psi(r)}{dr} = \sinh\psi(r) \tag{2}$$

where the distance from the particle center $\tilde{r}$ is normalized on the Debye length

$$\kappa^{-1} = \sqrt{\frac{2\varepsilon RT}{F^2 C_0}} \tag{3}$$

$r = \tilde{r}/\kappa^{-1}$ and $\tilde{r}$ are the dimensionless and dimensional polar radii, $\psi(r) = F\tilde{\psi}(\tilde{r})/RT$ and $\tilde{\psi}(\tilde{r})$ are the distributions of the equilibrium dimensionless and dimensional electric potentials, ε is the dielectric permittivity of the medium, F is the Faraday constant, R is the gas constant, T is the absolute temperature, and C_0 is the bulk concentration of electrolyte.

The electrical potential $\psi(r)$ satisfies two boundary conditions:

At the particle surface it equals to the surface potential ψ_S:

$$\psi(r = a) = \psi_S, \tag{4}$$

and with account of symmetry of the system at the external boundary of the cell its derivative is equal to zero:

$$\left.\frac{d\psi}{dr}\right|_{r=b} = 0, \tag{5}$$

where $a = \tilde{a}/\kappa^{-1}$, $b = \tilde{b}/\kappa^{-1}$ are dimensionless radii of a particle and a cell.

In the case of low surface potentials Eq. (2) can be presented according to the Debye approximation $\psi_S < 1$ [23] as

$$\frac{d^2\psi(r)}{dr^2} + \frac{2}{r}\frac{d\psi(r)}{dr} = \psi(r), \tag{6}$$

which can be easy solved using the change of the variable

$$\psi(r) = \frac{\phi(r)}{r} \tag{7}$$

With account of conditions (4) and (5) the solution of Eq. (6) takes the following simple form

$$\psi(r) = \psi_S \frac{a}{r}\left(\frac{e^r + \frac{b-1}{b+1}e^{2b-r}}{e^a + \frac{b-1}{b+1}e^{2b-a}}\right) \tag{8}$$

The approximations, which will be used for solution of Eq. (2) in the case of high surface potential, are more complicated than the Debye approximation.

3. Two-layer cell model at high surface potentials

The transition from one-layer cell model (Fig. 1) to two-layer one (Fig. 2) at

$$\psi_S \gg 1, \tag{9}$$

is based on the characteristics of the potential and ion distributions in the electric double layers at their overlapping.

The internal layer ($a < r < b^*$) is a region of high potentials, where the concentration of counterions prevails over the concentration of coions and the solution of the Poisson–Boltzmann equation can be simplified using the model of the excluded coions (see, for example [7]). To ensure sufficient accuracy of the description of the potential distribution in this layer its local values should satisfy as a minimum the condition $\psi(r) > 2$.

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