

Double layer interaction between charged parallel plates using a modified Poisson–Boltzmann equation to include size effects and ion specificity

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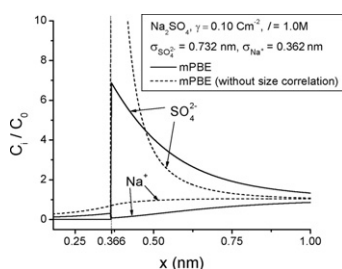
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HIGHLIGHTS

- ▶ We include ion-size correlation together with ion-colloid dispersion interaction effects into Poisson–Boltzmann equation.
- ▶ A formulation using differential-algebraic equations allows a fast and stable numerical solution of this non-linear problem.
- ▶ We show here that ion-size correlation is very important for bigger and more polarizable counterions.
- ▶ In several examples, we also show the importance of ion-size asymmetries in adequately modeling colloidal systems.

GRAPHICAL ABSTRACT



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ABSTRACT

We present calculations of double layer interaction between charged plates taking into account size effects on colloidal systems. Those are modeled using a modified version of Poisson–Boltzmann equation, including non-electrostatic interactions due to the size and the polarizability of each ion. The van der Waals interactions and size effects can properly describe ion specificity as observed experimentally in many colloidal systems. The differential-algebraic mathematical structure is used to solve the modified Poisson–Boltzmann equation. The DASSL code is recursively applied using a Newton–Raphson method to solve the corresponding boundary-value problem. Density profiles around colloidal particles are calculated for different charged-particles immersed in various electrolytes aqueous solutions. From these profiles, we could calculate the pressure (interaction) between the plates. The influence of charge and size asymmetries of ions on density profiles are studied in different solutions. Results show the adequacy of this modified form of the Poisson–Boltzmann equation and the proposed mathematic procedure to solve the needed equations, describing several properties of colloidal systems and ion size correlation.

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1. Introduction

The electrical double layer (EDL) interaction between charged surfaces immersed in electrolyte solutions is an important aspect on colloid and interface science. The use of Gouy [1] and Chapman

[2] theory to define the ion distribution on double layer leads to the classical Poisson–Boltzmann equation (PBE). On this classical approach, the ions are pointlike charges in thermodynamic equilibrium without statistical fluctuations and immersed in a continuum medium with specified dielectric constant.

Although widely used to describe electrolyte solutions, the classical PBE has several limitations. After a rigorous analysis based on Statistical Mechanics, Kirkwood [3] stated that this limitations are associated with the neglect of an exclusion volume term and an

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electrostatic fluctuation term [4]. Despite the relative success on prediction of ion distribution in the vicinity of flat and spherical surfaces, the classical approach tends to overestimate the ion concentration around a charged surface, particularly for high surface charges and multivalent electrolytes. This effect is mainly caused by the absence of excluded-volume correlations [5–7].

Since Stern [8], aware of the limitations of Gouy–Chapman (GC) theory, stated that there should also be a compact ionic layer adsorbed near the surface, several attempts have been proposed to include volume effects in EDL theory. One of the first proposals in accounting excluded volume effects in PBE was via a lattice based approach, commonly referred as Langmuir type corrections [9,10]. Later works has extended and improved this approach, developing modified versions of PBE for engineering applications [5,11–13]. An alternative way to treat this problem is using equations of state (EoS) based on liquid-state theory for hard sphere mixtures. The use of Boublik–Mansoori–Carnahan–Starling–Leland (BMCSL) EoS [14,15] on GC theory allows the inclusion of size correlation terms as excess chemical potentials, which takes into account the size asymmetries of each ion in EDL calculations [16–19]. As the excess chemical potentials is a continuum function valid for the whole EDL, it is not necessary to limit an excluded volume layer (a Stern layer), and the size effect appears naturally.

In this paper we present pressure and ion density profiles calculations between a pair of charged parallel plates, in which we follow Lue’s approach [16] to take into account the ion size correlations by using the BMCSL EoS. In addition to the size effects, we also include dispersion potentials that act between ions and surfaces [20–22], which originates by the fact that ions have different polarizabilities than surrounding water. With these two modifications, an improved modified Poisson–Boltzmann equation (mPBE) is used. Because the size correlation contribution is a collective effect, the resulting mPBE constitutes a differential-algebraic equation, whose numerical solution can be directly obtained from the well-established computer code DASSL [23].

This paper is organized as follows. In Section 2 we present the methodology employed in modeling charged parallel plates via the proposed mPBE, the numerical procedure to solve the resulting differential-algebraic problem and how we calculate the pressure between the two plates. In Section 3 we present the main numerical results obtained. Then we show some conclusions in Section 4.

2. Methodology

2.1. Modeling of charged parallel plates

As the colloidal macroparticles typically have sizes much larger than the ions, in general, when the macroparticles local radius of curvature is large compared to the double layer thickness, it is reasonable to assume that the ions “see” the surface like a plane (flat) charged surface [24,25]. Thus, we estimate the interaction between two colloidal particles as if two equally charged parallel plates immersed in an electrolyte aqueous solution and separated by a distance L . We assume that the two plates have the same uniformly distributed charge densities (γ). The solvent is a continuum medium with dielectric constant (ϵ) equal to 78.5 (dielectric constant of water solvent). The opposite charge ions α and β are treated as hard spheres with diameters σ_α and σ_β . Fig. 1 presents a cartoon of the system.

Because the ions are treated as hard spheres, they cannot penetrate into the colloid surface, so there is a cutoff distance corresponding to smaller ion radius ($x_{cutoff} = \sigma_\alpha/2$) for the case in where $\sigma_\alpha < \sigma_\beta$. For $\sigma_\alpha \neq \sigma_\beta$, there are regions where only the smaller ion can be present. These regions are limited by the vertical

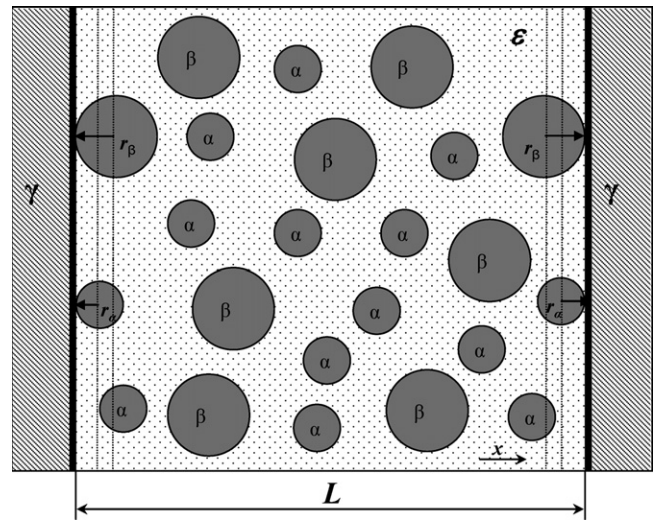


Fig. 1. Modeling of parallel plates with charge density γ , separated by a distance L and immersed in a dielectric medium (ϵ) composed by ions α and β with opposite charges and radius $r_\alpha = \sigma_\alpha/2$ and $r_\beta = \sigma_\beta/2$. In the region limited by the vertical dotted lines ($r_\alpha \leq x \leq r_\beta$ or $L - r_\beta \leq x \leq L - r_\alpha$), $c_\alpha \neq 0$ and $c_\beta = 0$.

dotted lines in Fig. 1 and corresponds to the ranges $\sigma_\alpha/2 \leq x \leq \sigma_\beta/2$ and $L - \sigma_\beta/2 \leq x \leq L - \sigma_\alpha/2$, where the concentration of the larger ion vanishes ($c_\beta = 0$), and the system consist only of the smaller ion ($c_\alpha \neq 0$). This represents a discontinuity in numerical solution obtained, as we discuss in Section 2.3.

2.2. Modified Poisson–Boltzmann equation (mPBE)

Here we present a modified PB equation that accounts for both the size and polarizability of each ion. The attractive contribution from ion–colloid dispersion potential enhances the ion size effect. Because the main purpose of this paper is to analyze the effects of ion size correlation and asymmetries, we neglect other important interactions, such as electrostatic correlations [26–28], polarization free energy and hydrophobic cavitation energy [28,29], ion hydration forces [30,31], and image effects [32].

Despite these approximations, we use in our calculations ion sizes that are recently estimated by Ninham’s group [33,34], based on ion hydration calculations for chaotropic and cosmotropic ions (as shown in Section 3). Therefore, although ion hydration potentials are neglected and water is structureless, hydration effects are indirectly included in our model when we use ion sizes that are consistent with them.

The modified Poisson–Boltzmann equation (mPBE) for two equally charged parallel plates is, in cartesian coordinates:

$$\frac{d^2 y}{dx^2} = -\frac{e}{\epsilon \epsilon_0} \sum_i z_i c_i(x) \quad \text{for } i = \alpha, \beta \quad (1)$$

$$\left. \left(\frac{dy}{dx} \right) \right|_{x_{min}} = -\frac{e\gamma}{\epsilon \epsilon_0 k_B T}, \quad \left. \left(\frac{dy}{dx} \right) \right|_{x=L/2} = 0 \quad (2)$$

where e is the elementary charge, ϵ is the dielectric constant of the solvent, ϵ_0 is the vacuum permittivity, y is the dimensionless electrical potential ($y = e\psi/k_B T$), k_B is the Boltzmann constant, T is the system temperature, and $x_{min} = x_{cutoff}$ is the cutoff distance.

The expressions in Eq. (2) represent the two boundary conditions. The first one is derived from Gauss law and is used when the charge surface density is specified. The second one is obtained from the symmetry due to equally charged plates. The expression of the density profile $c_i(x)$ is derived from the invariance of chemical potential of each ion along the electric double layer, taking

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