



# Asymmetric electrostatic properties of an electric double layer: a generalized Poisson–Boltzmann approach taking into account non-uniform size effects and water polarization



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## ABSTRACT

We theoretically study electrostatic properties of electric double layer using a generalized Poisson–Boltzmann approach taking into account the orientational ordering of water dipoles and the excluded volume effect of water molecules as well as those of positive and negative ions with different sizes in electrolyte solution.

Our approach enables one to predict that the number densities of water molecules, counterions and coions and the permittivity of electrolyte solution close to a charged surface, asymmetrically vary depending on both of sign and magnitude of the surface charge density and the volume of counterion. We treat several phenomena in more detail. Firstly, an increase in the volume of counterions and an increase in the surface charge density can cause the position of the minimum number density of water molecules to be farther from the charged surface. Secondly, width of the range of voltage in which the properties at the charged surface symmetrically vary decreases with increasing bulk salt concentration. In addition, we show that the excluded volume effect of water molecules and the orientational ordering of water dipoles can lead to early onset and lowering of the maximum of electric capacitance according to surface voltage. Our approach and results can be applied to describing electrostatic properties of biological membranes and electric double layer capacitor for which excluded volume effects of water molecules and ions with different sizes may be important.

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## 1. Introduction

The concept of electric double layer was first presented by Herman von Helmholtz [1] before more than one century. Since then many researchers have developed realistic theories of electric double layer to solve various problems of biology, medicine, colloid science and electrochemistry such as the binding of charged ligands to the membrane surface, the interactions of vesicles with the membrane, osteoblast attachment to biomaterials, fundamental nucleic acid processes, RNA folding, and differential capacitance of electric double layer capacitor [2–5].

To correctly represent electrostatic properties of electric double layer, a number of computational approaches such as Monte Carlo method and numerical solutions of integral equations [6–9] were introduced, but they involve more complicated calculations than for the Poisson–Boltzmann (PB) approach.

However, the original PB approach proposed by Gouy and Chapman [10,11] doesn't consider the finite volumes of ions in electrolyte and it is known that the approach heavily overestimates

the ionic concentrations close to charged surfaces in electrolyte. As an early attempt to eliminate such a shortcoming of the original PB approach, Stern [12] considered the finite size effect of ions by combining the Helmholtz model with the Gouy–Chapman model. To include volume effects of ions directly into the PB approach, Bikerman [13] empirically modified Boltzmann distribution by correcting ion concentrations for the volume excluded by all ions.

In [14–19], the authors considered finite volumes of ions and water molecules within lattice statistical mechanics approach. The assumption of the same size of ions and water molecules in electrolyte has been common to their work. Although this assumption does properly work in many situations, ionic transport across narrow channels and ionic adsorption in objects of subnanometer size cannot be described by means of the assumption. For example, when the size of a negative ion is larger than one of a positive ion, negative ionic transport across narrow channels of biological membranes or pores of electrode of electric double layer capacitor will hardly proceed.

Modified PB approaches using lattice statistics [20–22] were developed for considering the difference in sizes of positive and negative ions. For this purpose, in [20], a lattice in which one cell can contain several ions was used. In [21], the authors semiempirically extended a modified PB equation to the case of an asymmetric salt. Recently, in [22], the authors assumed that the lattice cell size was an integer number of times smaller than a linear dimension of ion.

In fact, the Booth model [23,24] is well-known for generalization of the Onsager-Kirkwood-Fröhlich permittivity model [25,26] in the saturation regime of orientational ordering of water dipoles, but the model doesn't consider the sizes of both ions and water molecules in electrolyte solution.

In [27–30,32], the authors took into account the excluded volume effect of water molecules and the orientational ordering of water dipoles together with the excluded volume effect of ions in the modification of the PB approach using lattice statistics. In particular, the authors described that the permittivity of an electrolyte solution near a strongly charged surface may be heavily decreased by orientational ordering of water dipoles and depletion of water molecules [28–30]. In their approach, each particle occupies one cell of lattice based on the assumption that the ions and water molecules have the same excluded volume, which allowed the PB equations to have analytical and intuitive solutions. However, in cases where effects of difference in excluded volumes of water molecules and ions may be important, for example, where the electric capacitance is asymmetric due to the difference in sizes of positive and negative ions [22], a more general approach taking into account the effects is needed.

In this paper we will incorporate not only the asymmetric size effect of ions in electrolyte but also both the orientational ordering of water dipoles and excluded volume effect of water molecules into the Poisson-Boltzmann approach. In a word, our approach generalizes that of [28] to include non-uniform ionic sizes. We introduce a lattice statistics where more than one cell can be occupied by each ion as in [22] and also by each water molecule for considering effects of different excluded volumes of ions and water molecules. We show that electrostatic properties of electrolyte solution close to a charged surface aren't symmetric in positive and negative surface charge densities of the charged surface. We study effects of the volume of counterion and sign and magnitude of the surface voltage on electrostatic properties of the electrolyte solution. Finally, an early onset and lowering of the maximum of electric capacitance are predicted.

## 2. The generalized Poisson-Boltzmann approach

We consider an electrolyte solution composed of multivalent ions and water molecules in contact with a charged planar surface, where a positive ion has charge  $+ze_0$  and a negative ion has charge  $-ze_0$ . The total free energy  $F$  can be written in terms of the local electrostatic potential  $\psi(r)$  and the number densities of ions  $c_+(r)$ ,  $c_-(r)$  and water molecules  $c_w(r) = \langle \rho(\omega, r) \rangle_\omega$ .

$$F = \int d\mathbf{r} \left( -\frac{\varepsilon_0 \varepsilon E^2}{2} + e_0 z \psi (c_+ - c_-) + \langle \rho(\omega) \rangle \gamma p_0 E \cos \omega \right)_\omega - \mu_+ c_+ - \mu_- c_- - \langle \mu_w(\omega) \rho(\omega) \rangle_\omega - Ts \quad (1)$$

where  $\langle f(\omega) \rangle_\omega = \int f(\omega) 2\pi \sin(\omega) d\omega$  in which  $\omega$  is the angle between the vector  $\mathbf{p}$  and the normal to the charged surface. Here  $\mathbf{p}$  is the dipole moment of water molecules and  $\mathbf{E}$  is the electric field strength. The first term is the self energy of the electrostatic field, where  $\varepsilon$  equals  $n^2$  and  $n = 1.33$  is the refractive index of water. The next term corresponds to the electrostatic energy of the ions in the

electrolyte solution, where  $e_0$  is the elementary charge. The third one represents the electrostatic energy of water dipoles [28], where  $\gamma = (2 + n^2)/2$ ,  $p_0 = |\mathbf{p}|$  and  $E = |\mathbf{E}|$ . The next three terms are responsible for coupling the system to a bulk reservoir, where  $\mu_{+,-}$  are the chemical potentials of positive ions and negative ions and  $\mu_w(\omega)$  is the chemical potential of water dipoles with orientational angle  $\omega$ .  $T$  is the temperature and  $s$  is the entropy density.

Consider a unit volume of the electrolyte solution. The entropy density is the logarithm of the number of translational and orientational arrangements of non-interacting  $c_+$  positive ions,  $c_-$  negative ions and  $\rho(\omega_i) \Delta \Omega_i (i = 1 \dots N)$  water molecules, where  $\Delta \Omega_i = 2\pi \sin(\omega_i) \Delta \omega$  is an element of a solid angle and  $\Delta \omega = \pi/N$ . The positive ion, negative ion and water molecule occupy volumes of  $V_+$ ,  $V_-$  and  $V_w$ , respectively.

Within a lattice statistics approach each particle in the solution occupies more than one cell of a lattice as in [22]. Considering translational arrangements of ions and orientational ordering of water dipoles, the number of arrangements can be calculated as follows. As in [22], we first place  $c_+$  positive ions of the volume  $V_+$  and then  $c_-$  negative ones of the volume  $V_-$  in the lattice. Finally, taking into account the orientational ordering of water dipoles, we put in  $\rho(\omega_i) (i = 0, 1, \dots)$  water molecules of the volume  $V_w$  in the lattice. The number of arrangements  $W$  is written as

$$W = \frac{c_s (c_s - 1 \cdot v_+) \dots (c_s - (c_+ - 1)v_+)}{c_+!} \times \frac{(c_s - c_+ v_\pm) \dots (c_s - c_+ v_\pm - (c_- - 1)v_-)}{c_-!} \times \frac{(c_s - c_+ v_+ - c_- v_-) \dots v_w}{\lim_{N \rightarrow \infty} \prod_{i=1}^N \rho(\omega_i) \Delta \Omega_i!} \quad (2)$$

where  $v_{+,-,w} = V_{+,-,w}/a^3$  are the numbers of cells that the positive ion, negative ion and water molecule occupy, respectively.  $c_s = 1/a^3$  is the number of cells per unit volume and  $a$  denotes the linear dimension of one cell.

From the standpoint of physics the entropy density should be symmetric in  $+$  and  $-$ . For this purpose, we assume that the positive(negative) ion excludes  $v_\pm = (v_+ + v_-)/2$  for the negative(positive) ion.

Expanding the logarithms of factorials using Stirlings formula, we obtain the expression for the entropy density,  $s = k_B \ln W$ ,

$$\begin{aligned} \frac{s}{k_B} = \ln W = & -c_+ \ln a^3 - c_- \ln a^3 - \left( \frac{1 - c_+ V_+ - c_- V_-}{V_w} \right) \ln a^3 \\ & - c_+ \ln c_+ - c_- \ln c_- - \left( \frac{1}{V_+} - c_+ \right) \ln(1 - c_+ V_+) \\ & + \left( \frac{1}{V_-} - \frac{c_+ V_\pm}{V_-} \right) \\ & \times \ln(1 - c_+ V_\pm) - \left( \frac{1}{V_-} - \frac{c_+ V_\pm}{V_-} - c_- \right) \\ & \times \ln(1 - c_+ V_\pm - c_- V_-) - \left( \frac{1}{V_w} - \frac{c_+ V_+}{V_w} - \frac{c_- V_-}{V_w} \right) \\ & \times \ln(1 - c_+ V_+ - c_- V_-) - \lim_{N \rightarrow \infty} \sum_{i=1}^N [\rho(\omega_i) \Delta \Omega_i \ln \Delta \Omega_i \\ & + \rho(\omega_i) \Delta \Omega_i \ln \rho(\omega_i) - \rho(\omega_i) \Delta \Omega_i], \quad (3) \end{aligned}$$

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