



# Adsorption of large ions from an electrolyte solution: a modified Poisson–Boltzmann equation

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Received 12 January 2000

## Abstract

The behavior of electrolyte solutions close to a charged surface is studied theoretically. A modified Poisson–Boltzmann equation that takes into account the volume excluded by the ions in addition to the electrostatic interactions is presented. In a formal lattice gas formalism the modified Poisson–Boltzmann equation can be obtained from a mean-field approximation of the partition function. In an alternative phenomenological approach, the same equation can be derived by including the entropy of the solvent molecules in the free energy. In order to visualize the effect of steric repulsion, a simple case of a single, highly charged, flat surface is discussed. This situation resembles recent adsorption experiments of large ions onto a charged monolayer. A simple criterion for the importance of the steric effects is expressed in terms of the surface charge density and the size of the ions. It is shown that when these effects are important a saturated layer is formed near the surface. A modified Grahame equation relating the ion concentration at the surface to the surface charge density is obtained. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Electrolyte solutions; Ion adsorption; Fluid/fluid interfaces; Stern layer; Langmuir monolayers

## 1. Introduction

The Poisson–Boltzmann equation is the main tool for studying the behavior of ionic solutions [1–5]. Its main advantages are its simplicity, which allows for analytical solutions in simple cases, and its surprisingly good agreement with experiments. Aqueous solutions of small and macro-ions are of interest from an industrial point of view (e.g. colloidal suspensions [6]) and as an important component in biological systems (e.g. DNA, charged membranes). Therefore, the Poisson–

Boltzmann approach was applied to many situations. Of particular interest are: (i) adsorption of ions to flat surfaces [7,8]; (ii) ion distribution around a charge cylinder and the so-called *Manning condensation* [9–14]; and (iii) ion distribution around a charged sphere and the so-called *charge renormalization* [12,15].

In its simpler form, the linearized Poisson–Boltzmann equation leads to the Debye–Hückel expression, thus providing a simple description of screening effects in terms of the Debye–Hückel screening length [16,17]. The success of the Poisson–Boltzmann approach is quite impressive in view of the various approximations that are included in its derivation: it is a mean field approach that totally neglects correlations and all specific (non-electrostatic) interactions between the ions including the ionic finite size.

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Nevertheless, despite the success of the Poisson–Boltzmann approach in describing a wide range of systems, it has been known for a long time to have some limitations in several cases: (i) the phase transition of electrolyte solutions [18], (ii) the adsorption of charged ions to highly charged surfaces [19–26], and (iii) the attractive interactions that can be observed between equally charged surfaces in the presence of multivalent counterions [27,28]. Consequently, there have been numerous attempts to improve upon the standard Poisson–Boltzmann approach [29–39].

In this study we focus on the second case, where highly charged surfaces attract a large amount of free ions from the solution. At high ion densities achieved close to the surface, short-range ion–ion interactions become comparable to the Coulomb interaction and they can no longer be neglected. In particular, the ion density is bounded by the maximum value that is obtained when the ions are closely packed. Recently, Cupvillier et al. [23–25] have provided an experimental setup that clearly demonstrates this situation. In their experiments large tungstic acid ions (diameter of about 10 Å) were adsorbed onto a charged monolayer spread at the air/water interface (Fig. 1). The insoluble (Langmuir) monolayer consists of charged amphiphilic molecules having two moieties: a charged head group favoring the water side of the interface, and a hydrocarbon tail favoring the air side. The surface charge density can be controlled continuously by changing the monolayer density through a lateral surface pressure. In the experiments, a large discrepancy was found between the measured ion concentration near the surface and the high values anticipated by the Poisson–Boltzmann approach.

Our aim in this study is to include the finite size of the ions in the Poisson–Boltzmann approach and study

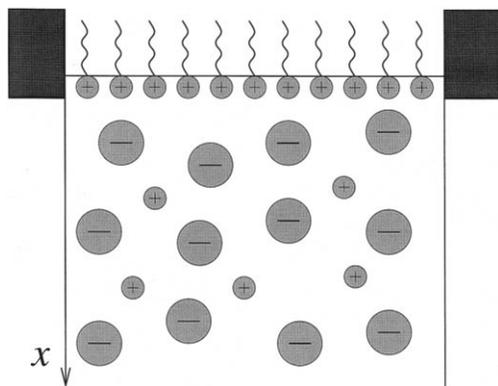


Fig. 1. Schematic view of the adsorption of large ions to a charged monolayer [23]. The surface charge is carried by amphiphilic molecules that are confined to the air/water interface. The surface charge density can be varied continuously by changing the area per amphiphilic molecule.

how the ion distribution close to charged surfaces is affected. The standard way of including the finite size of the ions in the Poisson–Boltzmann approach is to define a narrow layer close to the surface as impenetrable to the ions. This layer is usually referred to as the *Stern layer* [40] and its width is equal to the ion radius. Outside this layer the regular Poisson–Boltzmann equation is implemented. In our approach, a modified Poisson–Boltzmann equation is derived where the steric forces lead to saturation of the ion density at high potentials. This way, the width of the saturated layer depends also on the surface charge and is not limited a priori to only one counterion layer [41].

In Section 2 the modified Poisson–Boltzmann equation is derived for different combinations of ion valencies. Two derivations are presented: first, a systematic path integral approach where the ions are put on a discrete lattice, and second, a phenomenological free energy formulation where the excluded volume effect is added through the entropy of the solvent. This equation is then implemented in Section 3 to study the adsorption of large ions to flat surfaces.

## 2. The modified Poisson–Boltzmann equation

### 2.1. Lattice gas formulation

Consider an aqueous solution of charged ions. For simplicity we will assume that both co-ions and counter-ions have the same size  $a$ . This assumption can be justified when all the surface charges are of the same sign, since only counterions are then attracted to the surface and reach high charge densities.

For the valencies of the ions we will consider three cases: (i) a symmetric  $z:z$  electrolyte, (ii) an asymmetric  $1:z$  electrolyte, and (iii)  $z$ -valent counterions without additional salt. The different cases will be used to study the application of the modified equation in different physical systems.

For a symmetric  $z:z$  electrolyte the solution contains two charged carriers, with charges equal to  $\pm ze$ . In order to derive the free energy we will use a discrete lattice gas formulation. In this approach, the charge carriers are placed on a three dimensional cubic lattice where the dimensions of a single cell are  $a \times a \times a$  (Fig. 2). Thus, by dividing space into discrete cells (lattice sites) and limiting the occupation of each cell to a single ion we introduce a short-range repulsion between the ions. The size of a cell represents the volume of an ion up to a numerical prefactor.

In order to describe the occupation of cells by ions we assign to each cell  $j$ , which is located at  $\mathbf{r}_j$ , a spin-like variables  $s_j$ . This variable can have one of three values:  $s_j = 0$  if the cell is empty (occupied by a water molecule), and  $s_j = \pm 1$  according to the sign of the ion

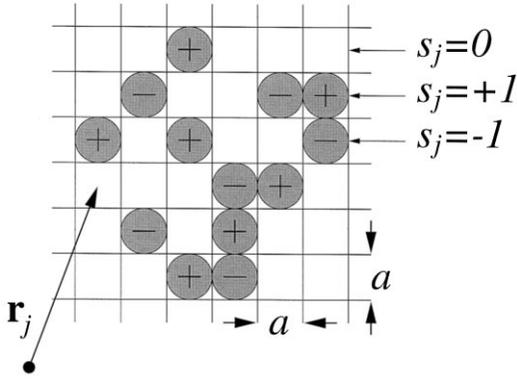


Fig. 2. Schematic view of an electrolyte on a lattice model. The lattice cells are located at  $\mathbf{r}_j$  and assigned a spin-like variable  $s_j = 0, \pm 1$ .

that occupies the cell. The partition function of the system can now be written in the form [42–46]

$$Z = \sum_{s_j=0, \pm 1} \exp\left(-\frac{\beta}{2} z^2 e^2 \sum_{j, j'} s_j v_c(\mathbf{r}_j - \mathbf{r}_{j'}) s_{j'} + \sum_j \beta \mu_j s_j^2\right) \quad (1)$$

The first term in the exponent is the electrostatic energy, where  $v_c(\mathbf{r}) = 1/\varepsilon|\mathbf{r}|$  is the Coulomb interaction. The second term is the chemical potential term where  $\mu_j = \mu_+$  for the positive ions ( $s_j = +1$ ) and  $\mu_j = \mu_-$  for the negative ions ( $s_j = -1$ ).

The charge density operator can be expressed in terms of the spin variables as

$$\hat{\rho}_c(\mathbf{r}) = \sum_j z e s_j \delta(\mathbf{r} - \mathbf{r}_j) \quad (2)$$

It is then useful to introduce the density field  $\rho_c(\mathbf{r})$  and the conjugate field  $\varphi_c(\mathbf{r})$  through the identity

$$1 = \int \mathcal{D}\rho_c \delta[\rho_c(\mathbf{r}) - \hat{\rho}_c(\mathbf{r})] = \int \mathcal{D}\rho_c \mathcal{D}\varphi_c \exp\left(i\beta \int \mathbf{dr} \rho_c \varphi_c - i\beta z e \sum_j s_j \varphi_c(\mathbf{r}_j)\right) \quad (3)$$

where  $\int \mathcal{D}\rho_c$  is a functional integral over the values of  $\rho_c$  at all space points  $\mathbf{r}$ . It can be viewed as the continuum limit of multiple integrals over the values of  $\rho_c$  at different points in space [47]:

$$\prod_j \int d\rho_c(\mathbf{r}_j) \rightarrow \int \mathcal{D}\rho_c \quad (4)$$

using the above identity is equivalent to the Hubbard–Stratonovitch transformation [48] and leads to

$$Z = \int \mathcal{D}\rho_c \mathcal{D}\varphi_c \exp\left(-\frac{\beta}{2} \int \mathbf{dr} \mathbf{dr}' \rho_c(\mathbf{r}) v_c(\mathbf{r} - \mathbf{r}') \rho_c(\mathbf{r}') + i\beta \int \mathbf{dr} \rho_c(\mathbf{r}) \varphi_c(\mathbf{r})\right) \times \sum_{s_j=0, \pm 1} \exp\left(-i\beta z e \sum_j s_j \varphi_c(\mathbf{r}_j) + \sum_j \beta \mu_j s_j^2\right) \quad (5)$$

Recall that  $\mathbf{r}_j$  are the discrete coordinates of the lattice site while  $\mathbf{r}, \mathbf{r}'$  are continuous spatial coordinates. It is now possible to trace over the allowed values of the spin-like variables,  $s_j = 0, \pm 1$  (last line in Eq. (5)). In the continuum limit, where physical properties vary on length scales much larger than the size of a single site, the sum over the lattice sites can be replaced by a continuous integral over space and the partition function simplifies to

$$Z = \int \mathcal{D}\rho_c \mathcal{D}\varphi_c \exp\left(-\frac{\beta}{2} \int \mathbf{dr} \mathbf{dr}' \rho_c(\mathbf{r}) v_c(\mathbf{r} - \mathbf{r}') \rho_c(\mathbf{r}') + i\beta \int \mathbf{dr} \rho_c(\mathbf{r}) \varphi_c(\mathbf{r}) + \frac{1}{a^3} \int \mathbf{dr} \ln\{1 + e^{\beta\mu_+ - iz\beta e\varphi_c(\mathbf{r})} + e^{\beta\mu_- + iz\beta e\varphi_c(\mathbf{r})}\}\right) \quad (6)$$

Since the exponential is quadratic in  $\rho_c$ , its functional integral can be performed.

$$Z = \int \mathcal{D}\varphi_c \exp\left(-\frac{\beta\varepsilon}{8\pi} \int \mathbf{dr} |\nabla\varphi_c|^2 + \frac{1}{a^3} \int \mathbf{dr} \ln\{1 + e^{\beta\mu_+ - iz\beta e\varphi_c(\mathbf{r})} + e^{\beta\mu_- + iz\beta e\varphi_c(\mathbf{r})}\}\right) \quad (7)$$

The chemical potentials  $\mu_{\pm}$  are related to the total number of positive and negative ions in the solutions through

$$N_{\pm} = \frac{1}{Z} \frac{\partial Z}{\partial(\beta\mu_{\pm})} = \left\langle \frac{1}{a^3} \int \mathbf{dr} \frac{e^{\beta\mu_{\pm} \mp iz\beta e\varphi_c(\mathbf{r})}}{1 + e^{\beta\mu_+ - iz\beta e\varphi_c(\mathbf{r})} + e^{\beta\mu_- + iz\beta e\varphi_c(\mathbf{r})}} \right\rangle \quad (8)$$

Where  $\langle \mathcal{O} \rangle$  denotes the grand canonical average of the operator  $\mathcal{O}$ .

In the bulk, the total number of positive and negative ions is equal,  $N_+ = N_- = N/2$ . It is useful to define the volume fraction occupied by both the co- and counterions as  $\phi_0 = Na^3/V = 2c_b a^3$  where  $V$  is the total volume and  $c_b$  is the bulk concentration of the electrolyte. In the thermodynamic limit  $N, V \rightarrow \infty$  while  $c_b$  and  $\phi_0$  remain finite. Using Eq. (8) the chemical potentials can be expressed in terms of  $\phi_0$ :

$$e^{\beta\mu_+} = e^{\beta\mu_-} = \frac{1}{2} \frac{\phi_0}{1 - \phi_0} \quad (9)$$

In the mean field approximation, the partition function is approximated by the value of the functional integral at its saddle point  $\psi(\mathbf{r}) \equiv i\varphi_c$ . The free energy of the system is then given by

$$\begin{aligned} \frac{F}{k_B T} &= -\ln Z \\ &= -\frac{\beta\varepsilon}{8\pi} \int d\mathbf{r} |\nabla\psi|^2 \\ &\quad - \frac{1}{a^3} \int d\mathbf{r} \ln \left\{ 1 + \frac{\phi_0}{1-\phi_0} \cosh[\beta z e \psi(\mathbf{r})] \right\} \end{aligned} \quad (10)$$

where  $\psi(\mathbf{r})$  satisfies the modified Poisson–Boltzmann (MPB) equation for a symmetric  $z:z$  electrolyte [26]:

$$\nabla^2\psi = \frac{8\pi z e}{\varepsilon} \frac{c_b \sinh(z\beta e\psi)}{1-\phi_0 + \phi_0 \cosh(z\beta e\psi)} \quad (11)$$

In the zero size limit,  $a \rightarrow 0$ , (namely  $\phi_0 \rightarrow 0$  while  $c_b$  remains fixed) the above equation reduces to the regular Poisson–Boltzmann equation:

$$\nabla^2\psi = \frac{8\pi z e}{\varepsilon} c_b \sinh(z\beta e\psi) \quad (12)$$

For an asymmetric  $1:z$  electrolyte the derivation is very similar and the MPB equation is:

$$\nabla^2\psi = \frac{4\pi z e c_b}{\varepsilon} \frac{e^{z\beta e\psi} - e^{-\beta e\psi}}{1-\phi_0 + \phi_0(e^{z\beta e\psi} + z e^{-\beta e\psi})/(z+1)} \quad (13)$$

where  $\phi_0 = (z+1)a^3 c_b$  is the combined bulk volume fraction of the positive and negative ions.

Finally, if the solution is salt free and contains only negative counterions of valency  $-|z|$ , the MPB equation becomes

$$\nabla^2\psi = \frac{4\pi z e c_0}{\varepsilon} \frac{e^{z\beta e\psi}}{1-\phi_0 + \phi_0 e^{z\beta e\psi}} \quad (14)$$

where  $\phi_0 = a^3 c_0$  is the volume fraction at an arbitrary reference point  $\mathbf{r}_0$  where  $\psi(\mathbf{r}_0) = 0$  and  $c(\mathbf{r}_0) = c_0$ . Note that as in the usual Poisson–Boltzmann treatment, in the absence of salt the reference point of zero potential does not lie at infinity. The salt-free system contains only the counterions, which neutralize the surface charge. Since the surface is taken to be infinite in its size, the potential does not go to zero as  $x \rightarrow \infty$ , but it diverges to  $-\infty$ . Physically this divergence is not a problem because the electric field and counterion density tend to zero at large distances.

## 2.2. Phenomenological free energy derivation

The MPB equation (Eqs. (11), (13) and (14)) can also be derived from a phenomenological free energy [26]. Let us consider again the symmetric  $z:z$  case. This is done by expressing the free energy of the system  $F = U_{el} - TS$  in terms of the local electrostatic potential  $\psi(\mathbf{r})$  and the ion concentrations  $c^\pm(\mathbf{r})$ . The electrostatic contribution is

$$U_{el} = \int d\mathbf{r} \left[ -\frac{\varepsilon}{8\pi} |\nabla\psi|^2 + z e c^+ \psi - z e c^- \psi - \mu_+ c^+ - \mu_- c^- \right] \quad (15)$$

The first term is the self-energy of the electric field and the next two terms are the electrostatic energies of the ions. The last two terms couple the system to a bulk reservoir, where  $\mu_\pm$  are the chemical potentials of the ions.

The entropic contribution is

$$\begin{aligned} -TS &= \frac{k_B T}{a^3} \int d\mathbf{r} [c^+ a^3 \ln(c^+ a^3) + c^- a^3 \ln(c^- a^3) \\ &\quad + (1 - c^+ a^3 - c^- a^3) \ln(1 - c^+ a^3 - c^- a^3)] \end{aligned} \quad (16)$$

The first two terms represent the translational entropy of the positive and negative ions, whereas the last term is the entropy of the solvent molecules. It is this last term that is responsible for the modification of the Poisson–Boltzmann equation. Note that it is also possible to include additional short-range (non-electrostatic) interaction terms in the modified Poisson–Boltzmann (MPB) free energy [38], but we will not consider them here.

Minimizing the total free energy with respect to  $\psi$  and  $c^\pm$  yields the Poisson equation

$$\nabla^2\psi = -\frac{4\pi}{\varepsilon} [z e c^+(\mathbf{r}) - z e c^-(\mathbf{r})] \quad (17)$$

where the ion concentrations are given by

$$c^\pm = \frac{c_b e^{\mp\beta z e\psi}}{1-\phi_0 + \phi_0 \cosh(\beta z e\psi)} \quad (18)$$

Here, as before,  $\phi_0 = 2c_b a^3$  denotes the bulk volume fraction of the small ions. Combining the above two expressions recovers the MPB equation (Eq. (11)). The same approach can also be applied in the derivation of Eqs. (13) and (14) [26]. A similar expression was suggested in the 1950s by Eigen [19] and more recently by Kralj-Iglić and Iglič [20–22]. Similar ionic distributions can be also obtained for solid electrolytes [49–51].

This approach deviates significantly from the original Poisson–Boltzmann equation for large electrostatic potentials  $|\beta e\psi| \gg 1$ . In particular, the ionic concentration is unbound in the standard Poisson–Boltzmann approach, whereas here it is always bound by  $1/a^3$  ('close packing') as can be seen from Eqs. (11) and (13) and Eq. (14). This effect is important close to strongly charged surfaces immersed in an electrolyte solution.

Note that for high positive potentials,  $\beta e\psi \gg 1$ , the contribution of the positive ions is negligible and the negative ion concentration follows a distribution reminiscent of the Fermi–Dirac distribution

$$c^-(\mathbf{r}) \rightarrow \frac{1}{a^3} \frac{1}{1 + e^{-\beta(z e \psi + \mu)}} \quad (19)$$

where the excluded volume interaction plays the role of the Pauli exclusion principle, and  $\mu = \mu_-$  is the chemical potential of the negative ions.

The effect of the additional entropy term and the fact that it limits the concentration of ions near the surface can be demonstrated by the following simple argument: consider a nearly saturated region near a highly charged (positive) surface where  $c^- a^3 \rightarrow 1$ . On one hand, the system can gain entropy by pushing solvent molecules in between the positive ions. On the other hand, diluting the saturated layer costs electrostatic energy. Altogether, the excess free energy per unit volume of diluting the saturated layer with a volume fraction  $\eta = 1 - c^- a^3$  of solvent molecules is:

$$\Delta f \simeq \frac{k_B T}{a^3} \eta (\ln \eta - 1) + \frac{z e |\psi_s|}{a^3} \eta \quad (20)$$

$\psi_s$  is the electric potential near the surface. The balance between these two terms results in an optimal non-zero dilution equal to

$$\eta^* \simeq e^{-z \beta e |\psi_s|} \quad (21)$$

and the free energy gain due to this dilution is

$$\Delta f \simeq - \frac{k_B T}{a^3} \eta^* \quad (22)$$

We conclude that entropy will always drive solvent molecules into the saturated layer. Although at high surface charge densities their amount becomes exponentially small.

### 3. Adsorption to a flat surface

The MPB equation can help to interpret the adsorption experiments of Cuvillier et al. [23–25]. In their experiments large (diameter of about 10 Å) negative multivalent ( $z = 3$  or  $z = 4$ ) ions were adsorbed onto a positively charged langmuir monolayer (Fig. 1). The large polyanions such as phosphotungstic acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) were dissolved in an aqueous subphase and attracted to a cationic Langmuir monolayer such as a fatty amine surfactant ( $\text{C}_{20}\text{H}_{41}\text{-NH}_2$ ), spread at the water/air interface.

Consider, therefore, a solution containing an asymmetric (1:z) electrolyte in contact with a single planar surface of charge density  $\sigma > 0$ . Assuming that the system is homogeneous in the lateral directions, the modified Poisson–Boltzmann equation (Eq. (13)) reads:

$$y''(x) = 4\pi l_B z c_b \frac{e^{zy} - e^{-y}}{1 - \phi_0 + \phi_0 (e^{zy} + z e^{-y}) / (z + 1)} \quad (23)$$

where  $y(x) = \beta e \psi(x)$  is the reduced electrostatic potential as function of the distance  $x$  from the surface and

$l_B = e^2 / \epsilon k_B T$  is the Bjerrum length  $l_B = 7$  Å for an aqueous solution at room temperature. Eq. (23) can be solved numerically yielding the electrostatic potential and ion concentration profiles as a function of the distance from the surface.

Typical results are presented in Fig. 3 for various values of the ion size  $a$  together with the solution of the original ( $a = 0$ ) Poisson–Boltzmann equation. In Fig. 3a the negative counterion concentrations are plotted and in Fig. 3b the electric potential. Since at high surface charge densities the positive co-ion concentration is small near the surface, only the negative ion profiles are shown.

Clearly, the ionic concentration saturates to its maximal value in the vicinity of the charged surface. This should be contrasted with the original Poisson–Boltzmann scheme, which leads to extremely high and unphysical values of  $c_s^- \equiv c^-(0)$ , especially for multivalent ions. In the saturated region, the ionic concentration tends to  $1/a^3$ , leading to more pronounced deviations from Poisson–Boltzmann for larger ions. Note, that in contrast with the Stern layer model, the width of the saturated layer (Fig. 3a) is not strictly equal to  $a$ . As will be demonstrated below, it depends not only on the parameter  $a$  but also on the surface charge density  $\sigma$ .

In the saturated layer the right-hand side of Eq. (13) becomes a constant, and the electrostatic potential is quadratic

$$\psi(x) \simeq \psi_s - \frac{4\pi\sigma}{\epsilon} x + \frac{2\pi z e}{\epsilon a^3} x^2 \quad (24)$$

where  $\psi_s$  is the surface potential and the boundary condition  $\psi'|_s = -4\pi\sigma/\epsilon$  is satisfied. As can be seen in Fig. 3b, the parabolic curve is a good approximation for  $\psi(x)$  close to the surface. The width of the saturated layer  $l^*$  is not strictly equal to  $a$ . It can be easily estimated from Eq. (24) to be

$$l^* \simeq a^3 \sigma / z e \quad (25)$$

in qualitative agreement with Fig. 3a.

The surface potential  $\psi_s$  can be calculated in a closed analytical form using the first integral of Eq. (23), with a single assumption that the positive ions (co-ions) density is negligible at the surface

$$\begin{aligned} \psi_s &\simeq \frac{k_B T}{z e} \{ \ln[e^{\zeta_1} - (1 - \phi_0)] - \ln(c_b a^3) \} \\ &\simeq \frac{k_B T}{z e} \{ \zeta_1 - \ln(c_b a^3) \} \end{aligned} \quad (26)$$

where

$$\zeta_1 \equiv \frac{2\pi a^3 \sigma^2}{\epsilon k_B T} \quad (27)$$

The last approximation in Eq. (26) is valid only for high values of  $\zeta_1 \gg 1$ . The dimensionless parameters  $\zeta_1$

is a measure of the importance of excluded volume interactions. It can be written as a ratio between the volume of a single ion and an electrostatic volume

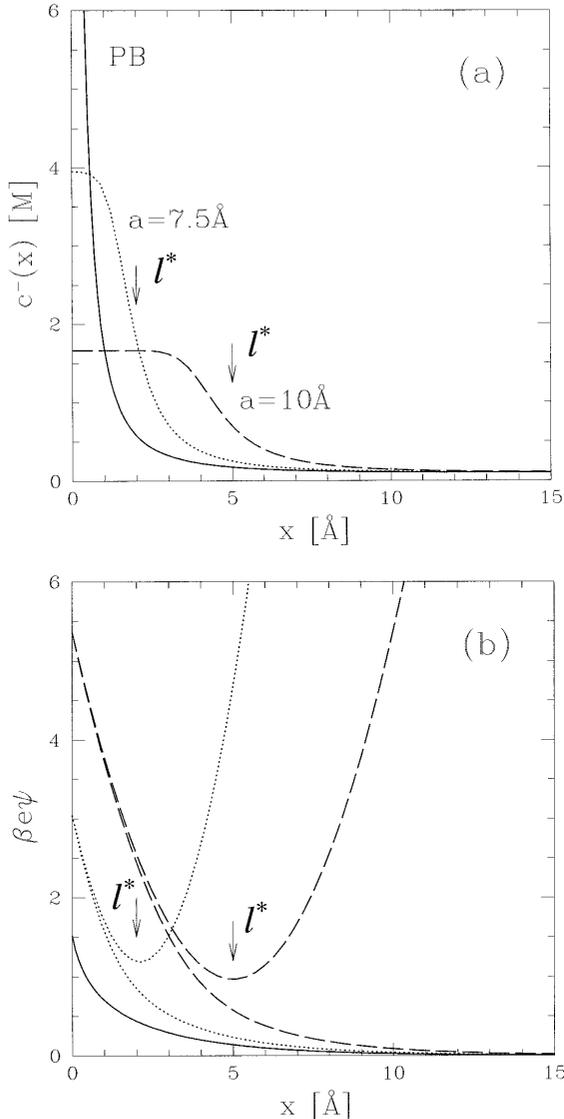


Fig. 3. (a) Concentration profiles of negative multivalent ions  $c^-(x)$  near a positively charged surface as obtained from the numerical solution of Eq. (23) for two different ion size  $a = 7.5$  Å (dotted line) and  $a = 10$  Å (dashed line). The saturated layer width  $l^* \simeq 2$  and  $5$  Å, respectively, is indicated by small arrows. The solid line represents the concentration profile of the standard Poisson–Boltzmann equation. (b) Calculated electrostatic potential profiles near the surface plotted together with the parabolic approximation (Eqs. (24) and (26)). The dotted, dashed and solid lines are as in (a). The bulk concentration is  $c_b = 0.1$  M for a  $1:z$  electrolyte with  $z = 4$ . The surface charge density  $\sigma$  is taken as one electron charge per  $50$  Å<sup>2</sup>. The aqueous solution with  $\varepsilon = 80$  is at room temperature so that the Bjerrum length is  $l_B = 7$  Å.

$$\zeta_1 \equiv \frac{a^3}{\Sigma \lambda_{GC}} \quad (28)$$

where  $\Sigma = e/|\sigma|$  is the area per surface charge, and  $\lambda_{GC} = \Sigma/(2\pi l_B) \propto 1/|\sigma|$  is the Gouy–Chapman length [52–54]. The characteristic width of a diffusive electrolyte layer near a charged surface in a salt-free solution is  $\lambda_{GC}/z$  while the volume per unit charge is also reduced by the same factor. Consequently,  $\zeta_1$  is dependent on  $z$ .

Similarly, the concentration of negative ions at the surface can be calculated leading to a modified Grahame equation [1]

$$c_s^- \simeq \frac{1}{a^3} [1 - (1 - \phi_0) e^{-\zeta_1}] \quad (29)$$

In the above equation, as in Eq. (26), the only additional approximation is to neglect the concentration  $c_s^+$  of the positive (co-)ions close to the surface. At low surface charge  $\zeta_1 \ll 1$ , and the ion concentration reduces to the Poisson–Boltzmann results

$$c_s^- = \frac{2\pi\sigma^2}{\varepsilon k_B T} + (1+z)c_b \quad (30)$$

but for high surface charge  $\zeta_1 \gg 1$ , the deviation from the Poisson–Boltzmann case is substantial.

The surface concentration of negative ions is depicted in Fig. 4a, where  $c_s^-$  is plotted as a function of the surface charge density,  $\sigma/e$ . Eq. (29) is presented for three different ions sizes and the original Poisson–Boltzmann case (Eq. (30)) is shown as well for comparison. At low surface charges the four curves are similar, but as the surface charge increases, the curves deviate from each other. The large ions deviate first and saturate to a lower surface concentration  $c_s^- \rightarrow 1/a^3$ . The deviation point corresponds to  $\zeta_1 \simeq 1$ . For  $a = 10$  Å this gives  $\sigma/e \simeq 0.005$  Å<sup>-2</sup> in qualitative agreement with Fig. 4a. It is interesting to note that the ionic concentration near the surface at high surface charge density depends only weakly on the bulk electrolyte concentration,  $c_b$ .

At high values of  $\zeta_1$ , the width of the saturated layer is of the order of  $l^*$  (Eq. (25)) and the amount of charge in the saturated layer can be estimated by

$$\sigma^* \simeq z e c_s^- l^* \simeq [1 - (1 - \phi_0) e^{-\zeta_1}] \sigma \quad (31)$$

In Fig. 4b the ratio between the ion charge density of the saturated layer  $\sigma^*$  and  $\sigma$  is plotted as function of the specific surface area per unit charge, as is often measured in experiments. At high surface charge densities (or equivalently, small surface area per unit charge) the saturated layer plays a dominant role in neutralizing the surface charge density. As the surface charge density is lowered, the width of the saturated layer decreases until it vanishes. This occurs when  $\zeta_1$  is of order unity, corresponding to  $\sigma^*/\sigma \simeq 1 - 1/e$  in the limit  $\phi_0 \ll 1$ . This crossover is indicated in Fig. 4b as a

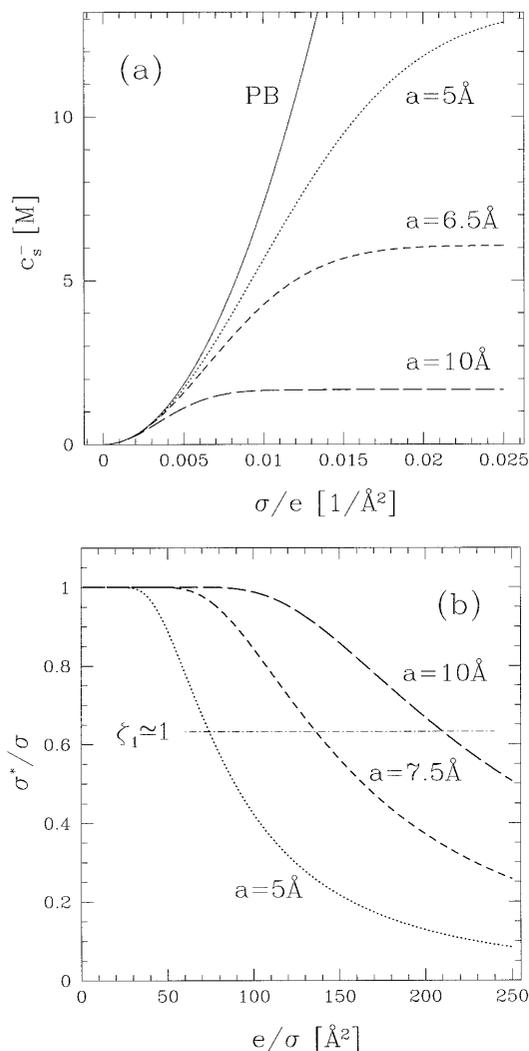


Fig. 4. (a) Concentration of counterions at the surface,  $c_s^- = c^-(0)$ , as a function of the surface charge density  $\sigma/e$  for different ions size,  $a$ . The Poisson–Boltzmann concentration is also plotted for comparison. (b) Ratio of the saturated layer charge density and the surface charge density,  $\sigma^*/\sigma = zec_s^- 1^*/\sigma$ , as a function of the specific surface area per unit charge,  $e/\sigma$ , for different ion sizes. The 1:z electrolyte bulk concentration is  $c_b = 1$  mM and the valency  $z = 4$ . The horizontal line indicates the crossover region  $\zeta_1 \approx 1$  in low salt concentrations.

horizontal line below which the saturated layer is no longer well defined. It should be noted that in our approach the counterions never over-compensate the surface charges, namely,  $\sigma^*/\sigma < 1$ .

In the experiments of Cuvillier et al. [23–25] the adsorbed ion density (per unit area) in the solution,  $\sigma^*$ , is measured by X-ray reflectivity. It is then related to the surface charge density  $\sigma$ , which is controlled by the Langmuir trough lateral pressure. The experiments show very clearly the presence of the steric effects of

these large ions (of estimated size of  $10\text{\AA}$ ). As the surface charge density increases,  $\sigma^*/\sigma$  decreases in accord with our findings (Fig. 4b) and in contrast to the original Poisson–Boltzmann approach. The experiments also show some evidence that the amount of charge in the adsorbed layer (per unit area) might exceed the original surface charge density and lead to over-compensation of surface charges [23–25]. Our approach does not yield such an effect because it does not include correlations between ions in solution, which are of particular importance to multivalent counterions. Additional ion–ion or ion–surface interactions may also be responsible for this effect.

The two different adsorption regimes are shown in Fig. 5 where the dividing line  $\zeta_1 = 1$  marks the onset of steric effects. We have seen that at low charge densities the parameter  $\zeta_1 \ll 1$  and our results coincide with those of the original Poisson–Boltzmann equation, which does not take into account the steric effects. On the other hand, when  $\zeta_1 \gg 1$ , corresponding to high surface charge densities or large ion sizes, steric effects are, indeed, important. The concentration of counterions cannot exceed its maximal value of close packing and this affects the surface potential and its dependence on the surface charge.

#### 4. Conclusions

In this work we have studied the effect of ion size on the density profiles of counterions near a charged sur-

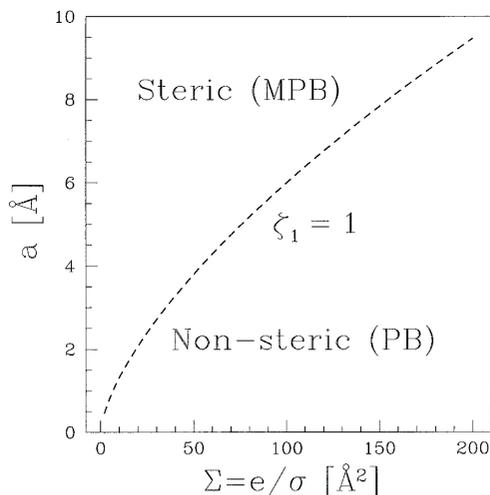


Fig. 5. Schematic diagram of the adsorption regimes of the large ions to a charged surface. The dashed line separates between the regime where steric effects are too weak to be relevant and the regime where the short-range ion–ion repulsion becomes important. The horizontal axis is the area per unit charge  $e/\sigma$  in  $\text{\AA}^2$  and the vertical axis is the ion size  $a$ .

face. For this purpose, an MPB equation was derived, which includes the short-range steric repulsion between ions in addition to the electrostatic interactions. A formal lattice gas derivation was presented as well as a phenomenological one. In the former derivation the steric repulsion results from the maximal occupancy of a single lattice site, while in the latter it stems from the translational entropy of the ions and solvent molecules. The two points of view are equivalent and result in the same MPB equation.

The MPB formalism was applied to a simple case of relatively large counterions adsorbing to a strongly charged surface. This model system corresponds to recent experiments [23–25] where multivalent large ions were adsorbed to a charged Langmuir monolayer. The advantage of the monolayer setup is the possibility to control the surface charge density via application of a surface pressure at the water/air interface.

We show that at high surface charge densities, in agreement with experiments, a saturated counterion layer is formed close to the surface. This is due to the fact that the ion concentration is limited by its maximal value, namely, close packing. This is in contrast with the standard Poisson–Boltzmann formalism where the ion concentration can be arbitrarily high.

The difference between the MPB and standard Poisson–Boltzmann formalism can be also expressed in terms of a modified Grahame equation relating the concentration of counterions at the surface to the surface charge density. This comparison introduces a dimensionless parameter  $\zeta_1 = a^3/\Sigma\lambda_{GC}$  where  $a$  is the ion size,  $\Sigma$  the specific area per surface charge and  $\lambda_{GC} = \Sigma/2\pi l_B$  the Gouy–Chapman length,  $l_B$  being the Bjerrum length. As long as  $\zeta_1 \lesssim 1$  the steric effects are weak. However, when  $\zeta_1 \gtrsim 1$  (large  $a$ , small  $\Sigma$ ) they cannot be neglected any more and saturation appears in the adsorbed layer.

The quadratic corrections to mean field theory presented here can be easily calculated. They correspond to the random phase approximation (RPA). In a homogeneous system, it can be shown that the effective charge–charge interactions are of the Debye–Hückel type with an unmodified screening length. In a non-uniform system (e.g. in the presence of a charged surface) the calculation is more involved. It requires knowledge of the analytical solution of the corresponding mean field equation [55].

Since the aim of this work was to identify and clarify the consequences of a single effect, namely the ionic size, we did not include additional contributions that might affect similar systems. Among these are specific ion–surface interaction, attractive ion–ion interactions and ion–ion correlations [27–38]. The latter are especially important for multivalent ions but their inclusion usually leads to complex integral equations where the underlying physics is not as transparent as in the MPB approach.

The MPB equation can be also applied to different geometries to study the adsorption to curved surfaces [56] and the interactions between charged surfaces in the presence of large ions.

## Acknowledgements

We wish to thank N. Cuvillier and F. Rondelez for sharing with us their experimental results prior to publication and for fruitful discussions. We also benefited from discussions and correspondence with H. Diamant, M.E. Fisher, C. Holm, A.A. Kornyshev, R. Netz, P. Sens and M. Urbakh. Partial support from the US-Israel Binational Foundation (BSF) under grant No. 98-00429, and the Israel Science Foundation founded by the Israel Academy of Sciences and Humanities — Centers of Excellence Program is gratefully acknowledged. One of us (HO) would like to thank the Sackler Institute of Solid State Physics (Tel Aviv University) for a travel grant. IB gratefully acknowledges the support of the Chateaubriand postdoctoral fellowship.

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