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# On the non-dominance of counterions in the 1:z planar electrical double layer of point-ions

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## ABSTRACT

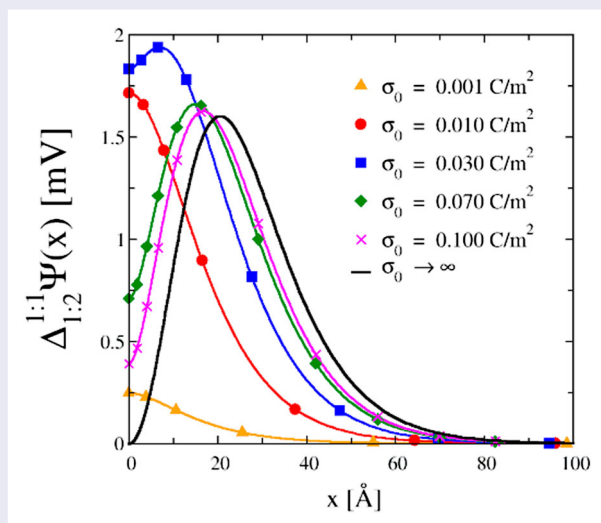
According to the dominance prescription of point-ions in the non-linear Poisson-Boltzmann theory, proposed by Valleau and Torrie almost 40 years ago, the microscopic and thermodynamic properties of an asymmetric binary electrolyte converge asymptotically to those of a completely symmetric electrolyte, in the limit of an infinite surface charge density of a planar electrode, if the properties of the counterions are the same in both instances. By using the Grahame equation and the non-linear Poisson-Boltzmann theory, we show here that this prescription is certainly *exact* for the mean electrostatic potential at the electrode's surface and for the capacitive compactness. Contrastingly, analytical and numerical solutions of the non-linear Poisson-Boltzmann equation show that, in the limit of an infinite surface charge density of the planar electrode, it is possible to observe finite differences between the local mean electrostatic potentials and electric fields associated to a 1:1 and a 1:z electrolyte at places near the electrode's surface. Thus, we prove here that even in the absence of ion correlations and ionic excluded volume effects, *the counterions do not fully dominate the structural properties in the entire electrical double layer in the non-linear Poisson-Boltzmann picture, which is confirmed through comparisons with new Monte Carlo simulations.*

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## 1. Introduction

The electrostatic and thermodynamic properties of charged colloids, such as macroions and electrified biomolecules, or electrodes immersed in an electrolytic solution are mainly determined by the spatial distribution of ions, which is the so-called electrical double layer.

A large number of experimental, theoretical, and simulation works have been performed since the last century in order to understand the microscopic and macroscopic properties of the electrical double layer in a wide variety of conditions [1,2]. This knowledge is very important to comprehend complex physicochemical and biological

processes, and to propose novel technological applications based on charged soft condensed matter.

On the other hand, almost 40 years ago Valleau and Torrie performed a theoretical inquiry, in the non-linear Poisson-Boltzmann framework, about the role of the ionic size-asymmetry in the electrolytic charge distribution of a binary mixture of valence-symmetric *semi-punctual* ions, next to a charged plane. In that study [3], they pointed out an apparently ‘obvious’ or expected fact later known as the dominance of the counterions in the electrical double layer. According to them, only counterions are found near the surface of a strongly charged colloid of either sign. Thus, in the limit of very strong electric fields, the ionic size-asymmetry between coions and counterions becomes irrelevant and the only important ion-size parameter is the effective radius of the counterions. In other words, and quoting those authors: ‘... When there is a substantial surface charge ... we expect the double layer properties of a dilute electrolyte to become similar to those of a completely symmetric electrolyte having an effective size equal to that of the counterion ...’. In such a scenario, the contribution of coions to the properties of the diffuse electrical double layer becomes negligible regarding the contribution of counterions. As a result, the properties and behaviour of coions at large electric fields are irrelevant in this classic description of the electrical double layer, whose characteristics are dominated or determined mainly by counterions. This mean field recipe led to many researchers to unfoundedly extend its validity to the case of genuine hard-sphere ions of arbitrary size and valence close to a charged surface [4–14], which corresponds to the so-called ‘unrestricted’ primitive model of the electrical double layer. The direct application of the dominance principle, stated by Valleau and Torrie exclusively in the non-linear Poisson-Boltzmann formalism, to the primitive model of colloidal systems is neither appropriate nor justified when ion correlations and ionic excluded volume effects are relevant. In this context, some of the present authors have shown in a couple of previous papers [15,16] that, precisely, and contrary to the common belief, the counterions do not dominate or determine the properties of the primitive model electrical double layer, due precisely to ion correlations and ionic excluded effects. In these articles it was found that, at large colloidal charges, the behaviour of the primitive model electrical double layer associated to a  $z_+z_-$  size-asymmetric electrolyte does not converge to that of a  $z_+z_-$  size-symmetric electrolyte when the properties of counterions (such as the ionic size, valence, and concentration) are the same in both electrolytes. That is, it has been evinced in such works that the characteristics of the coions in  $z_+z_-$  electrolytes, symmetric in valence and asymmetric in size, are relevant

and do matter for highly electrified colloids at high salt concentrations. Afterwards, some of the present authors have also shown that in the case of equisized  $1:z$  primitive model electrolytes with multivalent coions [17], the properties of the electric double layer do not converge in the limit of very large colloidal surface charge densities (as it would be expected according to the dominance of counterions in the classical non-linear Poisson-Boltzmann approach). In other words, it has been explicitly shown that, for equally sized  $1:z$  primitive model electrolytes, counterions do not dominate the properties of the ionic cloud around highly charged colloids when ion correlations and ionic excluded effects are taken into account consistently. These ingredients are missing in classical mean field descriptions, such as the non-linear Poisson-Boltzmann theory.

In summary, in the physical chemistry community, the complete dominance of counterions at a non-linear Poisson-Boltzmann level (when a fully asymmetric binary electrolyte is present) has been taken by granted without a rigorous proof. In this work, we are interested in analysing this hypothesis by using analytical equations and accurate numerical solutions of the non-linear Poisson-Boltzmann theory in planar geometry. As a result, we show here that the prescription of the dominance of counterions is certainly *exact* at the level of electrostatic properties of a  $1:z$  electrolyte such as the surface mean electrostatic potential  $\Psi_0$  and the capacitive compactness  $\tau_c$ . Nevertheless, we also explicitly demonstrate that the dominance of counterions is not necessarily true, in general, in the whole space at the level of the *local* mean electrostatic potential and electric field in the non-linear Poisson-Boltzmann picture.

## 2. Model system and theory

In this study, we consider a point-ions  $1:z$  ( $-1 : z_+$ ) electrolyte bathing a charged and infinite planar electrode with a positive bare surface charge density  $\sigma_0 > 0$ . Anions (counterions) and cations (coions) can approach up to the colloidal surface, where the surface mean electrostatic is  $\Psi_0$ . The non-linear Poisson-Boltzmann equation for the local mean electrostatic potential can be expressed in terms of the ionic profiles next to the charged electrode. On the other hand, and formally, the normalised ionic profile  $g_i(x)$  of the species  $i$  in planar geometry is related to the ionic potential of mean force  $W_i(x)$ :

$$\rho_i(x) = \rho_i^{\text{bulk}} g_i(x) = \rho_i^{\text{bulk}} e^{-W_i(x)/k_B T}, \quad (1)$$

where  $k_B$  is the Boltzmann constant and  $T$  is the absolute temperature of the system. The potential of mean force is the necessary work required to bring a charged particle

from infinite up to a distance  $x$ , where  $x$  is the perpendicular distance between a point in the three-dimensional space and the surface of the electrode. As a first approximation, the potential of mean force can be equated to the electrostatic energy  $W(x) = e_0 z_i \Psi(x)$ , where  $e_0$  is the protonic elementary charge,  $z_i$  is the valence of ions of species  $i$  and  $\Psi(x)$  is the mean electrostatic potential due to the charged surface and the electrolyte. If the ionic profiles, defined in terms of the mean electrostatic potential, are substituted in the Poisson equation,  $\nabla^2 \Psi(x) = -\rho_{el}(x)/(\varepsilon_0 \epsilon)$ , then the non-linear Poisson-Boltzmann equation is obtained

$$\nabla^2 \Psi(x) = -\frac{1}{\varepsilon_0 \epsilon} \sum_i \rho_i^{\text{bulk}} z_i e_0 \exp\left(-\frac{e_0 z_i \Psi(x)}{k_B T}\right). \quad (2)$$

The linear Poisson-Boltzmann equation can be obtained by linearising Equation (2). For a charge symmetric  $z_- : z_+$  electrolyte (with  $z_- = -z_+$ ) this linear approximation results in the following relation between the mean electrostatic potential at the electrode's surface  $\Psi_0$ , and the surface charge density  $\sigma_0$

$$\Psi_0 = \frac{\sigma_0}{\varepsilon_0 \epsilon \kappa_D} \quad (3)$$

in planar geometry. In this definition, the Debye length of the supporting electrolyte in bulk is defined as  $\lambda_D = 1/\kappa_D$  with

$$\kappa_D = \left( \frac{\sum_i \rho_i^{\text{bulk}} z_i^2 e_0^2}{\varepsilon_0 \epsilon k_B T} \right)^{\frac{1}{2}}. \quad (4)$$

Additionally, the corresponding integrated charge, electric field, and mean electrostatic potential can be written, in general, as [18]

$$\sigma(x) = \sigma_0 + \int_0^x \sum_i \rho_i^{\text{bulk}} g_i(t) e_0 z_i dt, \quad (5)$$

$$E(x) = \frac{\sigma(x)}{\varepsilon_0 \epsilon}, \quad (6)$$

and

$$\Psi(x) = \frac{e_0}{\varepsilon_0 \epsilon} \int_x^\infty (x-t) \left( \sum_{i=-,+} \rho_i^{\text{bulk}} z_i (g_i(t) - 1) \right) dt. \quad (7)$$

To our best knowledge, there are not exact analytical solutions of the non-linear Poisson-Boltzmann equation in the presence of charge-asymmetric  $-1 : z_+$  point-ions electrolytes, except for the 1:1 and 1:2 instances. Thus, numerical solutions of these equations are required. Note that instead of solving the differential equation associated to the non-linear Poisson-Boltzmann theory, we prefer to solve here the corresponding integral equations via

an efficient finite element approach. Detailed and explicit derivations of these equations in planar geometry can be found elsewhere [19, 20], so we will just briefly sketch them here.

The Ornstein-Zernike equations describing the ionic cloud around a single spherical macroion can be written as

$$h_{Mj}(r) = c_{Mj}(r) + \sum_{k=-,+} \rho_k^{\text{bulk}} \int h_{Mk}(t) c_{kj}(|\vec{r} - \vec{t}|) dV, \quad (8)$$

for  $j = +, -$ , and where  $h_{Mj}(r) = g_{Mj}(r) - 1$  are the total ionic correlation functions, and  $g_{Mj}(r)$  are the ionic radial distribution functions. The direct correlation functions between ions and the spherical colloid are specified by using the hypernetted-chain (HNC) closure  $c_{Mj}(r) = -\beta U_{Mj}(r) + h_{Mj}(r) - \ln[h_{Mj}(r) + 1]$ . If  $c_{kj}(|\vec{r} - \vec{t}|) = -\beta(z_k z_j e_0^2)/(4\pi \varepsilon_0 \epsilon |\vec{r} - \vec{t}|)$  is employed in the right-hand side of Equation (8), the integral equations version of the non-linear Poisson-Boltzmann theory is then obtained [19]. The integral form of the non-linear Poisson-Boltzmann equation for the electric double layer of a binary electrolyte next to a planar charged surface can be obtained from Equation (8) by taking the limit of a colloid with infinite radius [20]. These equations can be explicitly written as

$$g_i(x) = \exp \left\{ -z_i e_0 \beta \Psi_0 - z_i \left( \frac{e_0^2}{k_B T \varepsilon_0 \epsilon} \right) \int_b^\infty \times \left[ \sum_j z_j \rho_j^{\text{bulk}} g_j(t) \right] \mathcal{F}(x, t) dt \right\}, \quad (9)$$

for  $x \geq 0$ ,  $i, j = +, -$ ; where  $b$  is the closest approach distance between all point ions and the electrode's surface, and

$$\mathcal{F}(x, t) = \frac{(x+t) - |x-t|}{2}. \quad (10)$$

In previous works [18, 20], we have proposed the use of the capacity compactness  $\tau_c$  as an accurate and robust measure of the spatial extension of the electrical double layer next to a charged surface. Physically, the capacity compactness can be related to the separation distance between two electrodes associated to an effective electrical double layer capacitor. In general, the capacity compactness in planar geometry can be written as

$$\tau_c = \varepsilon_0 \epsilon \frac{\Psi_0}{\sigma_0}. \quad (11)$$

Note that, in the previous formula, the capacity compactness is measured from the surface of the charged electrode. By substituting Equation (3) in Equation (11), it is straightforward to obtain the capacitive compactness in the linear Poisson-Boltzmann or Debye-Hückel

theory. Following this linear theoretical description, the capacitive compactness  $\tau_c$  measured from the surface of the electrode is equal to the Debye length in planar geometry (as it is illustrated in Figure 2) in the absence of ionic specific adsorption and when the ionic closest approach distance between the point-ions and the colloidal surface is zero. Observe that in this approximation the capacitive compactness  $\tau_c$  is independent of the colloidal charge. A major limitation of the linear Poisson-Boltzmann or Debye-Hückel theory is that it is valid only in the limit of very weak charged surfaces. On the contrary, the non-linear Poisson-Boltzmann equation describing point-ions is valid at mild and even rather large surface charge densities. The capacitive compactness associated to this higher-order or non-linear description can be obtained from Equation (11) in planar geometry, if the mean electrostatic potential is calculated at the colloidal surface in terms of the corresponding ionic profiles via Equation (7). Alternative definitions of the capacitive compactness in planar, spherical and cylindrical geometries have been proposed, very recently, as the expected value of the electrostatic potential produced by an electrode immersed in a Coulombic fluid [21]. One advantage of these alternative definitions is that they are suitable to be used with more sophisticated theories (beyond the classical non-linear Poisson-Boltzmann theory) or molecular simulations to include the effects of the colloidal surface, ion correlations, ionic excluded volume effects, polarisation effects, ionic specific adsorption, etc.

On the other hand, the difference of the surface mean electrostatic potential and the capacitive compactness between a 1:1 and a 1: $z_+$  electrolyte in planar geometry can be calculated from the results of the corresponding numerical solution of the non-linear Poisson-Boltzmann equation. Nevertheless, it is worth noticing that these quantities can be also calculated analytically via the Grahame equation [22] as an alternative route. This analytical equation implicitly relates the surface mean electrostatic potential  $\Psi_0$  and the surface charge density  $\sigma_0$  of the electrode:

$$\frac{\text{sign}(y_0^{1:z_+})e_0\sigma_0}{\varepsilon_0 \varepsilon_0 k_B T} = \frac{1}{z_+ \lambda_D^{1:z_+}} \times \sqrt{\left[ \frac{2}{1+L} \right] \left[ \exp(-y_0^{1:z_+} z_+) \right] + \frac{\exp(y_0^{1:z_+} L z_+)}{L} - \left(1 + \frac{1}{L}\right)} \quad (12)$$

where  $L = \left| \frac{z_-}{z_+} \right|$  and  $y_0^{1:z_+} = \frac{e_0 \Psi_0^{1:z_+}}{k_B T}$ .

If we take the 1:1 system as a reference system, for a given  $\sigma_0$ , we can define  $-\Delta y_0 = y_0^{1:1} - y_0^{1:z_+}$  and

Equation (12) can be recast as

$$L \left[ \frac{2\alpha}{\beta} \cosh(y_0^{1:1}) + \frac{\gamma\beta - 2\alpha}{\beta} \right] = p \exp(-z_+ \Delta y_0) + q \exp(z_+ L \Delta y_0), \quad (13)$$

where  $\alpha = \left( \frac{z_+ \lambda_D^{1:z_+}}{\lambda_D^{1:1}} \right)^2$ ,  $\beta = \frac{2}{1+L}$ ,  $\gamma = 1 + \frac{1}{L}$ ,  $p = L \exp(-z_+ y_0^{1:1})$ ,  $q = \exp(z_+ L y_0^{1:1})$ .

The exponential functions in Equation (12) can be expanded in a Taylor series and, in a linear approximation,

$$\Delta y_0 = \frac{\eta - (p + q)}{z_+ (Lq - p)}, \quad (14)$$

where  $\eta = L \left[ \frac{2\alpha}{\beta} \cosh(y_0) + \left( \frac{\gamma\beta - 2\alpha}{\beta} \right) \right]$ .

In turn, in a quadratic approximation it is necessary to solve the following quadratic equation:

$$b_2 \Delta y_0^2 + b_1 \Delta y_0 + b_0 = 0, \quad (15)$$

where  $b_2 = \frac{z_+^2}{2} (qL^2 + p)$ ,  $b_1 = z_+ (qL - p)$ ,  $b_0 = (q + p) - \eta$ , and  $\eta = L \left[ \frac{2\alpha}{\beta} \cosh(y_0) + \left( \frac{\gamma\beta - 2\alpha}{\beta} \right) \right]$ .

The full solution of Equation (13) to find  $\Delta y_0$  can be performed numerically via a root finding algorithm such as the Newton-Raphson method.

In brief,  $\Delta y_0$  can be calculated analytically via a linear or a quadratic approximation of the exponentials of Equation (13); by solving numerically Equation (13) using, for instance, a Newton-Raphson scheme; or by numerically solving the non-linear Poisson-Boltzmann equation in integral form via the finite element method. Note that  $-\Delta y_0 = y_0^{1:1} - y_0^{1:z_+}$  allows us to know the difference of the surface mean electrostatic potential  $\Psi_0^{1:1} - \Psi_0^{1:z_+}$  and the difference of the capacitive compactness  $\tau_c^{1:1} - \tau_c^{1:z_+}$  between a 1:1 and a 1: $z_+$  ( $-1 : z_+$ ) electrolyte, when the properties of monovalent counterions are the same in the presence of multivalent coions.

In the case of 1:1 and 1:2 electrolytes there are analytical solutions of the Poisson-Boltzmann equation proposed by Ohshima [23]:

$$\Psi(x)_{1:1} = \frac{k_B T}{e_0} \ln \left[ \left( \frac{1 + \gamma e^{-\kappa x}}{1 - \gamma e^{-\kappa x}} \right)^2 \right] \quad (16)$$

$$\Psi(x)_{1:2} = \frac{k_B T}{e_0} \ln \left[ \frac{3}{2} \left( \frac{1 + \gamma' e^{-\kappa x}}{1 - \gamma' e^{-\kappa x}} \right)^2 - \frac{1}{2} \right], \quad (17)$$

where  $\kappa = \kappa_D y_0 = \frac{e_0 \Psi_0}{k_B T} \kappa = \kappa_D y_0 = \frac{e_0 \Psi_0}{k_B T}$ ,

$$\gamma = \frac{\exp(y_0/2) - 1}{\exp(y_0/2) + 1}, \quad (18)$$

and

$$\gamma' = \frac{\sqrt{\frac{2}{3} \exp(y_0) + \frac{1}{3}} - 1}{\sqrt{\frac{2}{3} \exp(y_0) + \frac{1}{3}} + 1}. \quad (19)$$

The limit of the mean electrostatic potential  $\Psi(x)$  and the electric field  $E(x)$  when the surface charge density goes to infinite is given by

$$\lim_{\Psi_0 \rightarrow \infty} \Psi(x)_{1:1} = \frac{k_B T}{e_0} \ln \left[ \left( \frac{1 + e^{-\kappa x}}{1 - e^{-\kappa x}} \right)^2 \right], \quad (20a)$$

$$\lim_{\Psi_0 \rightarrow \infty} \Psi(x)_{1:2} = \frac{k_B T}{e_0} \ln \left[ \frac{3}{2} \left( \frac{1 + e^{-\kappa x}}{1 - e^{-\kappa x}} \right)^2 - \frac{1}{2} \right], \quad (20b)$$

and

$$\lim_{\Psi_0 \rightarrow \infty} E(x)_{1:1} = 2 \frac{k_B T}{e_0} \frac{\kappa}{\tanh\left(\frac{\kappa x}{2}\right) [\cosh(\kappa x) + 1]}, \quad (21a)$$

$$\lim_{\Psi_0 \rightarrow \infty} E(x)_{1:2} = 3 \frac{k_B T}{e_0} \frac{\kappa}{\tanh\left(\frac{\kappa x}{2}\right) [\cosh(\kappa x) + 2]}. \quad (21b)$$

To our best knowledge, there are not additional analytical solutions of the non-linear Poisson-Boltzmann equation for 1:z electrolytes for  $z > 2$  in planar geometry. Thus, accurate numerical solutions have to be performed in such instances.

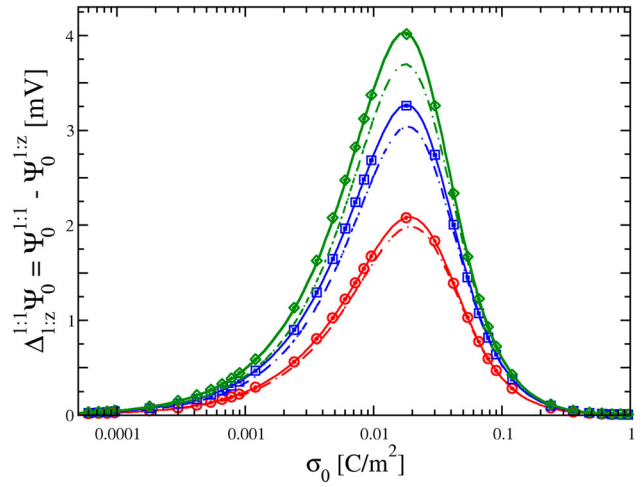
### 3. Results and discussion

Let us consider an infinite planar electrode in the presence of a 1:1 electrolyte as a reference system. We are interested in the difference of several electrostatic properties of the planar electrical double layer, such as the mean electrostatic potential, the electric field, and the capacitive compactness, in the presence of a 1:1 electrolyte or a 1:z ( $-1 : z_+$ ) electrolyte, when the concentration of monovalent counterions is the same in all cases and coions are multivalent. Note that under this condition, the concentration of coions is completely determined by the valence of multivalent coions due to the electroneutrality condition:

$$z_- \rho_-^{bulk} + z_+ \rho_+^{bulk} = 0. \quad (22)$$

Hereinafter, we consider that the charged electrode is bathed by a continuum aqueous solvent characterised by a dielectric constant  $\epsilon = 78.5$  at a temperature  $T = 298$  K in all instances.

In Figure 1, the difference of the surface mean electrostatic potential  $\Delta_{1:z}^{1:1} \Psi_0 = \Psi_0^{1:1} - \Psi_0^{1:z}$  is displayed,

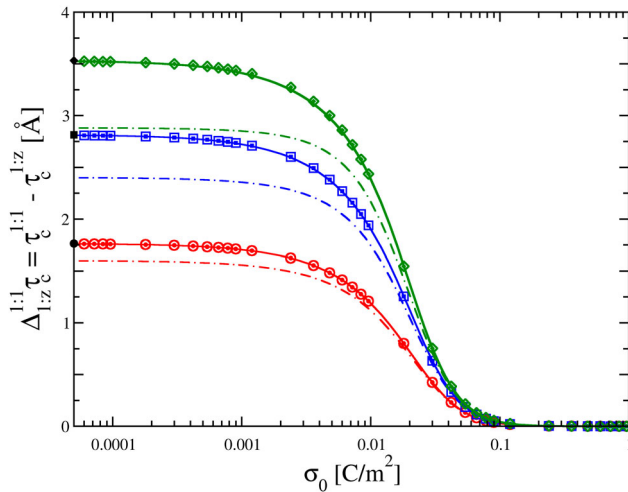


**Figure 1.** (Colour online) Difference of the surface mean electrostatic potential  $\Delta_{1:z}^{1:1} \Psi_0 = \Psi_0^{1:1} - \Psi_0^{1:z}$ , where  $\Psi_0^{1:1}$  and  $\Psi_0^{1:z}$  correspond to the mean electrostatic potential on the electrode's surface in the presence of a 1:1 and a 1:z electrolyte, respectively, when the monovalent counterions have the same concentration  $\rho_-^{bulk} = 0.1$  M in all instances. Red, blue, and green lines and symbols are associated to multivalent electrolytes with coion's valences  $z = z_+ = 2, 3, 4$ , respectively. The dot-dashed and solid lines are associated to the analytical solutions obtained by using a linear and a quadratic approximation of the exponentials in Equation (13), respectively. The empty and solid symbols represent the Newton-Raphson numerical solution of Equation (13) and the finite element method solution of the non-linear Poisson-Boltzmann integral equation, respectively.

where  $\Psi_0^{1:1}$  and  $\Psi_0^{1:z}$  are the surface mean electrostatic potentials in the presence of a 1:1 and a 1:z electrolyte, respectively, when the monovalent counterions have the same concentration  $\rho_-^{bulk} = 0.1$  M in all instances, and the valences of the multivalent coions are  $z_+ = 2, 3, 4$ . The difference  $\Delta_{1:z}^{1:1} \Psi_0$  was calculated analytically by using a linear and a quadratic approximation in the exponentials of Equation (13), numerically by solving Equation (13) via a Newton-Raphson algorithm, and by solving numerically the non-linear Poisson-Boltzmann equation via the finite element method. In this figure, it is observed that  $\Delta_{1:z}^{1:1} \Psi_0$  initially increases as a function of the surface charge density  $\sigma_0$ , reaches a maximum near  $0.02$  C/m<sup>2</sup> and, after this maximum,  $\Delta_{1:z}^{1:1} \Psi_0$  decreases monotonically to zero when  $\sigma_0$  goes to infinite. In addition, the maximum value of  $\Delta_{1:z}^{1:1} \Psi_0$  augments as a function of the valence of the multivalent coions. In terms of accuracy, both the quadratic approximation and the Newton-Raphson solution of Equation (13) reproduce the value of the  $\Delta_{1:z}^{1:1} \Psi_0$  predicted by the finite element method solution of the non-linear Poisson-Boltzmann equation for all 1:z electrolytes displayed. Contrastingly, the analytical linearised solution of Equation (13) underestimates the maximum of the  $\Delta_{1:z}^{1:1} \Psi_0$  and its accuracy

deteriorates when the valence of the multivalent coions increases. Nevertheless, the analytical linearised solution of Equation (13) converges to the same value displayed by the finite element solution of the non-linear Poisson-Boltzmann equation at large electric fields, reaching the zero value in the limit of an infinite surface charge density  $\sigma_0$ . These calculations demonstrate that the surface mean electrostatic potential  $\Psi_0$  converge to the same value for all 1:z electrolytes at large electric fields if the properties of counterions are the same in all instances, which corresponds precisely to the dominance of the counterions in the electrical double layer.

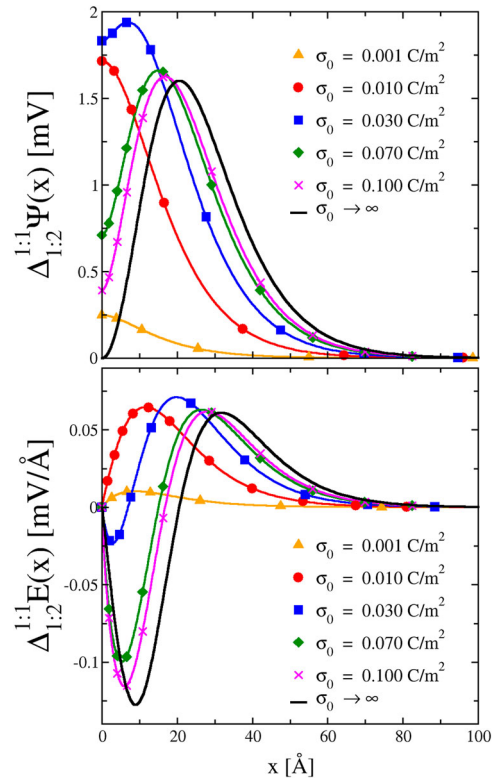
The difference of the capacitive compactness  $\Delta_{1:z}^{1:1} \tau_c = \tau_c^{1:1} - \tau_c^{1:z}$  as a function of  $\sigma_0$ , associated to the three cases of coion valences displayed in Figure 1, is shown in Figure 2. In this figure, it is observed that the maximum value of  $\Delta_{1:z}^{1:1} \tau_c$  is equal to the difference of the Debye length of the supporting electrolytes, and it occurs when the surface charge density  $\sigma_0$  goes to zero. When  $\sigma_0$  increases, it is observed that  $\Delta_{1:z}^{1:1} \tau_c$  decreases monotonically, eventually reaching a zero value in the limit of an infinite  $\sigma_0$ . These calculations evidence that the



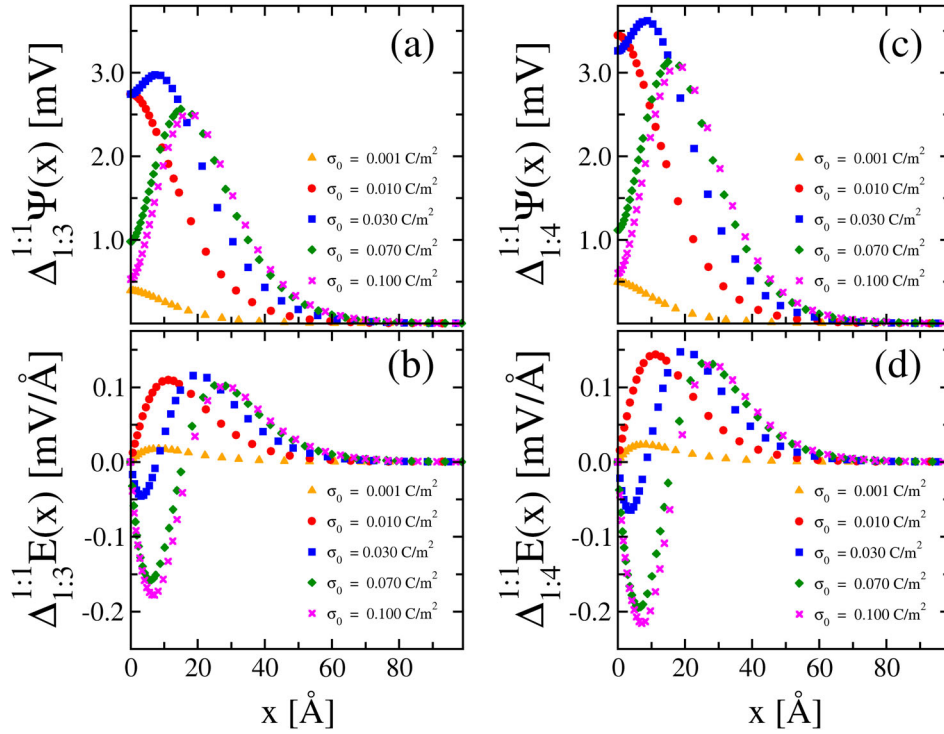
**Figure 2.** (Colour online) Difference of the capacitive compactness  $\Delta_{1:z}^{1:1} \tau_c = \tau_c^{1:1} - \tau_c^{1:z}$ , where  $\tau_c$  is given by Equation (11),  $\tau_c^{1:1}$  and  $\tau_c^{1:z}$  correspond to the capacitive compactness in the presence of a 1:1 and a 1:z electrolyte, respectively, and the monovalent counterions have the same concentration  $\rho_{-}^{\text{bulk}} = 0.1$  M in all instances. Red, blue, and green lines and symbols correspond to multivalent electrolytes with coion's valences  $z = z_+ = 2, 3, 4$ , respectively. The dot-dashed and solid lines are associated to the analytical solutions obtained by using a linear and a quadratic approximation of the exponentials in Equation (13), respectively. The empty and solid colour symbols represent the Newton-Raphson numerical solution of Equation (13) and the finite element method solution of the non-linear Poisson-Boltzmann integral equation, respectively. Black solid symbols correspond to the difference of the Debye lengths  $\lambda_D^{1:1} - \lambda_D^{1:z}$  of the bulk supporting electrolytes.

capacitive compactness  $\tau_c$  converges to the same value for all 1:z electrolytes at large electric fields if the properties of counterions are the same in all instances, which corresponds again to the dominance of the counterions for this electrostatic property of the electrical double layer.

Thus, we have proved that several electric properties associated to the surface of the electrode, such as the  $\Psi_0$  or  $\tau_c$  display the dominance of counterions proposed by Valleau and Torrie. In order to determine if the counterions' dominance also occurs at the level of the local mean electrostatic potential and electric field beyond the electrode's surface, let us calculate the corresponding differences in the presence of a 1:1 and a 1:z electrolyte at increasing surface charge densities  $\sigma_0$ , when the concentration of monovalent counterions is the same in all cases and coions are multivalent. These quantities, defined as  $\Delta_{1:z}^{1:1} \Psi(x) = \Psi^{1:1}(x) - \Psi^{1:z}(x)$  and  $\Delta_{1:z}^{1:1} E(x) = E^{1:1}(x) - E^{1:z}(x)$ , have been obtained by using the analytical solutions proposed by Ohshima [23] for  $z = z_+ = 1, 2$  for the non-linear Poisson-Boltzmann equation, and via numerical solutions of the non-linear Poisson-Boltzmann equation using the finite element



**Figure 3.** (Colour online) Differences  $\Delta_{1:z}^{1:1} \Psi(x)$  and  $\Delta_{1:z}^{1:1} E(x)$  as functions of  $x$ , for several values of  $\sigma_0$ . The solid lines display the analytical results obtained from the Ohshima formulas [23], while the solid symbols correspond to the numerical results obtained by solving the Poisson-Boltzmann equation using the finite element method. The fixed counterions' concentration is  $\rho_{-}^{\text{bulk}} = 0.1$  M in all instances.



**Figure 4.** (Colour online) Differences  $\Delta_{1:z}^{1:1}\Psi(x)$  and  $\Delta_{1:z}^{1:1}E(x)$  as functions of  $x$ , for the coion's valences  $z = z_+ = 3, 4$  and several values of  $\sigma_0$ . Panels (a) and (b) are for  $z = z_+ = 3$ , and panels (c) and (d) are for  $z = z_+ = 4$ . The solid symbols correspond to the numerical results obtained by solving the Poisson-Boltzmann equation using the finite element method. The fixed counterions' concentration is  $\rho_-^{\text{bulk}} = 0.1$  M in all instances.

method, and they are portrayed in Figure 3. In the case of  $\Delta_{1:2}^{1:1}\Psi(x)$ , it is noticed that the maximum value is located at the surface of the electrode at low values of the surface charge density  $\sigma_0$ . When  $\sigma_0$  increases, a new maximum appears near the surface of the electrode. In the limit of an infinite  $\sigma_0$  value,  $\Delta_{1:2}^{1:1}\Psi(0)$  goes to zero but  $\Delta_{1:2}^{1:1}\Psi(x)$  remains different from zero in the whole space except at the surface of the electrode, as already said, and very far away from the electrode. The  $\Delta_{1:2}^{1:1}E(x)$  displays a similar behaviour to that displayed by  $\Delta_{1:2}^{1:1}\Psi(x)$ , even though it is possible to observe now regions in which the sign of  $\Delta_{1:2}^{1:1}E(x)$  displayed at low  $\sigma_0$  values can be inverted. This change of sign is associated to the appearance of a maximum in  $\Delta_{1:2}^{1:1}\Psi(x)$  outside the surface of the electrode. In the limit of an infinite  $\sigma_0$  value,  $\Delta_{1:2}^{1:1}E(0)$  goes to zero whereas  $\Delta_{1:2}^{1:1}E(x)$  displays a value different from zero in the whole space except at the surface of the electrode and very far away from the electrode, as occurred with  $\Delta_{1:2}^{1:1}\Psi(x)$ . Thus, it is observed that the local mean electrostatic potential and electric field are different from zero, in general, in the whole space in the limit of an infinite surface charge density, except at the surface of the electrode and at an infinite distance from the electrode's surface.

These analytical and numerical results demonstrate that there are electrostatic properties of a 1:1 and a 1:2

electrolyte next to an infinite planar electrode, such as the mean electrostatic potential or the electric field in the whole space, that do not exactly converge to the same value when the surface charge density goes to infinite if the properties of counterions are the same in both supporting electrolytes. In other words, we have shown that the counterions do not fully dominate the electrical double layer structure in the non-linear Poisson-Boltzmann theory of point-ions.

In order to observe the effect of augmenting the valence of coions in 1:z electrolytes, Figure 4 presents the same quantities displayed in Figure 3 but now for a 1:3 and a 1:4 electrolyte, that is,  $\Delta_{1:z}^{1:1}\Psi(x) = \Psi^{1:1}(x) - \Psi^{1:z}(x)$  and  $\Delta_{1:z}^{1:1}E(x) = E^{1:1}(x) - E^{1:z}(x)$  are plotted for  $z = z_+ = 3, 4$ . In this instance, these differences were determined by solving numerically the non-linear Poisson-Boltzmann equation via the finite element method. For both electrolytes, the same behaviour already observed in Figure 3 is seen, except that now the magnitudes of the maxima and minima increase as a function of the valence of coions. In the limit of large surface charge densities, it is noted that  $\Delta_{1:1}^{1:z}\Psi(x)$  and  $\Delta_{1:1}^{1:z}E(x)$  are different from zero in the whole space, except perhaps at the surface of the electrode and very far away from the electrode's surface, which clarifies the non-dominance of counterions for



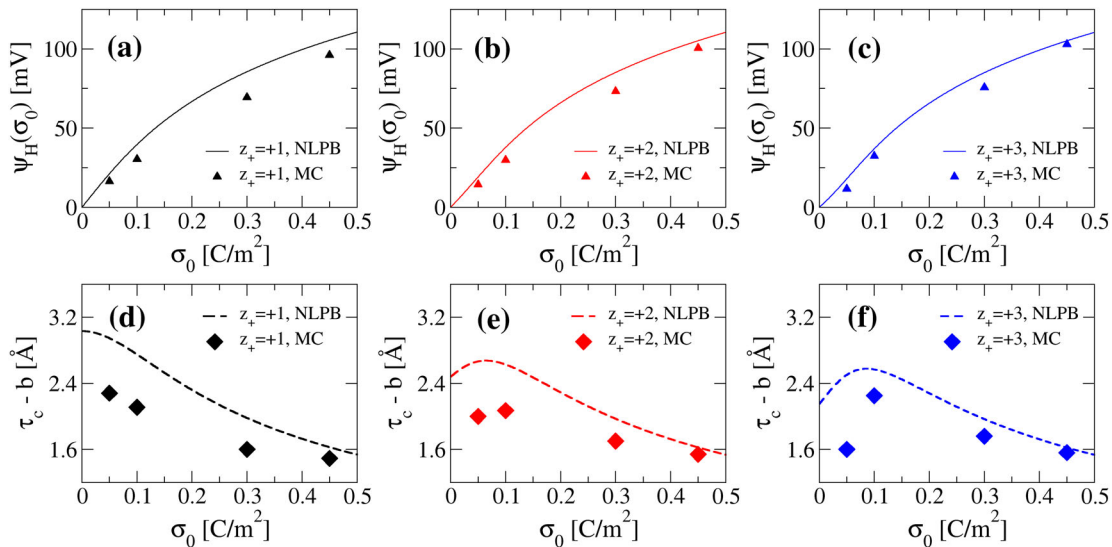
1:z electrolytes in the non-linear Poisson-Boltzmann picture.

#### 4. Validity and limitations of the current approach

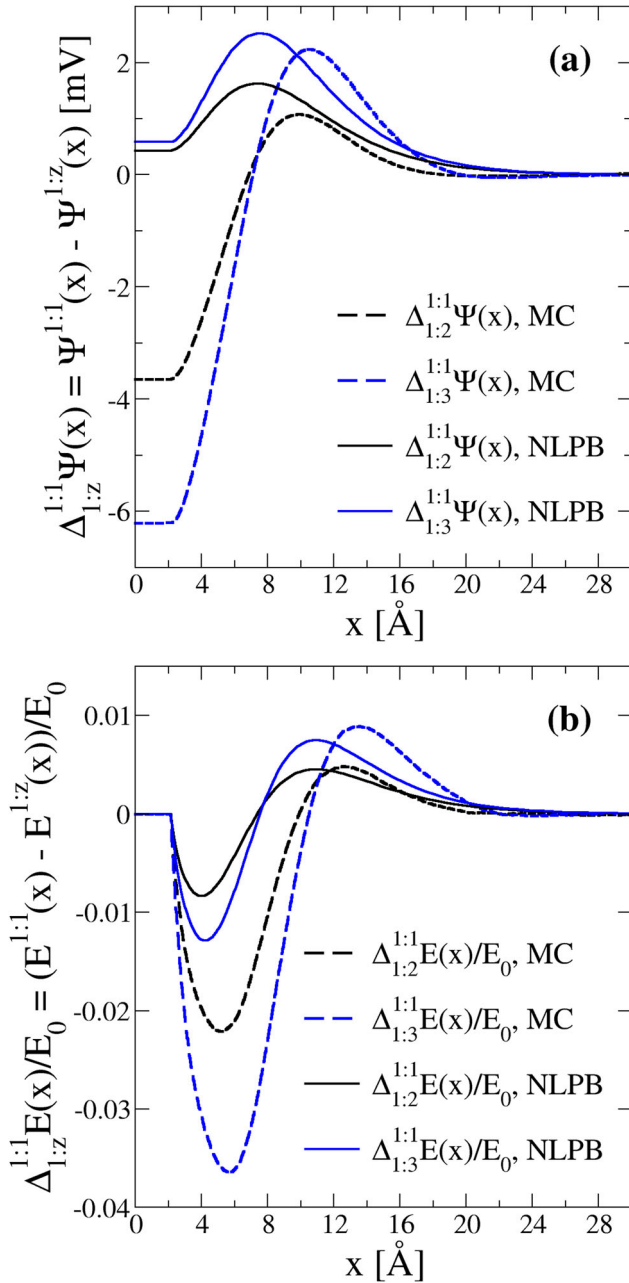
The non-linear Poisson-Boltzmann equation is a mean field theoretical approach, in which ionic correlations or ionic excluded volume effects are neglected. When these effects are taken into account, e.g. at the level of the primitive model, some of the present authors have shown that the dominance of counterions does not occur in the whole space, including the behaviour of the mean electrostatic potential at the surface and at the closest approach distance of ionic species regarding the colloidal surface (or Helmholtz plane) [15–17]. Thus, the fact that the non-linear Poisson-Boltzmann theory be able to predict a non-dominance of counterions at large bare electric fields is surprising and accentuates even more the relevance of this classic formalism. Complementary, other successful applications of the non-linear Poisson-Boltzmann theory include the estimation of the effective charge of macroions in solution [24–31] and the calculation of the capacitive compactness in the presence of monovalent counterions and multivalent coions [18]. In the first case, Alexander's prescription [24] was proposed as a practical method to estimate the effective charge of macroions dissolved in monovalent electrolytes by matching the tail of the mean electrostatic potential obtained via the non-linear Poisson-Boltzmann equation

regarding its linearised version in the cell model. Calculations based on this effective charge have displayed a good agreement regarding experimental osmotic pressure measurements. In the limit of very large bare surface charge densities, several authors have shown that the effective charge saturates in planar, spherical and cylindrical geometries [25–29], which has been also confirmed by primitive model Monte Carlo simulations [30]. Recently, the non-linear Poisson-Boltzmann equation has been used to improve the Alexander's prescription of the effective charge of macroions in solution via the Extended Point Charge (EPC) method [31] proposed by one of the present authors, which has been validated via primitive model molecular dynamics simulations of big macroions and small ions with size asymmetries of 250:1.

One important limitation of the non-linear Poisson-Boltzmann theory is its inability to predict the camel-back and bell shapes of the differential capacity in the strong coupling electrolyte regime, typically observed in ionic liquids [32]. In this regard, the non-linear Poisson-Boltzmann theory predicts a parabola or inverted bell shape for the differential capacity, which can be expected in the weak coupling electrolyte regime in the presence of 1:1 monovalent salts. On the other hand, and in order to test the suitability of the mean field non-linear Poisson-Boltzmann equation to model some other electrostatic properties of aqueous electrolytes with monovalent counterions at large bare surface charge densities  $\sigma_0$ , in Figure 5 we collate theoretical



**Figure 5.** (Colour online) Mean electrostatic potential at the Helmholtz plane  $\Psi_H$  and capacitive compactness  $\tau_c$ , in planar geometry, as a function of  $\sigma_0$ , for  $z = z_+ = 1, 2, 3$  and monovalent counterions of valence  $z_- = -1$ . The solid lines correspond to the numerical results obtained by numerically solving the non-linear Poisson-Boltzmann equation when the ionic closest approach distance is 2.125  $\text{\AA}$ . Solid symbols correspond to unpublished and published primitive model Monte Carlo simulations associated to Ref. [18], where the radius of 1:z equally sized primitive model ions is 2.125  $\text{\AA}$ . The fixed counterions' concentration is  $\rho_-^{\text{bulk}} = 1\text{M}$  and the continuum aqueous solvent is characterised by a dielectric constant  $\epsilon = 78.5$  at a temperature  $T = 298\text{K}$  in all instances.



**Figure 6.** (Colour online) Differences  $\Delta_{1:z}^{1:1}\Psi(x)$  and  $\Delta_{1:z}^{1:1}E(x)/E_0$  in planar geometry as a function of  $x$ , for a surface charge density  $\sigma_0 = 0.3 \text{ C/m}^2$  and  $z = z_+ = 2, 3$ . The solid lines correspond to the numerical results obtained by numerically solving the non-linear Poisson-Boltzmann equation when the ionic closest approach distance is  $2.125 \text{ \AA}$ . Dashed lines correspond to unpublished primitive model Monte Carlo simulations associated to Ref. [18], where the radius of  $1:z$  equally sized primitive model ions is  $2.125 \text{ \AA}$ . The fixed counterions' concentration is  $\rho_-^{\text{bulk}} = 1 \text{ M}$  and the continuum aqueous solvent is characterised by a dielectric constant  $\epsilon = 78.5$  at a temperature  $T = 298 \text{ K}$  in all instances.

non-linear Poisson-Boltzmann data with fresh primitive model Monte Carlo simulations results, for planar geometry, of the mean electrostatic potential at

the Helmholtz plane  $\Psi_H$  and of the capacitive compactness [18]  $\tau_c$ , as a function of  $\sigma_0$  for different  $1:z$  salts. Hereinafter, a  $1:z$  equally sized electrolyte with ionic radius  $b = 2.125 \text{ \AA}$  is considered. The concentration of monovalent counterions is always  $\rho_-^{\text{bulk}} = 1.0 \text{ M}$  and the concentration of coions of valence  $z$  is determined by the electroneutrality condition. Under these conditions, it is necessary to introduce in the non-linear Poisson theory an ionic closest approach distance regarding the electrode's surface, which defines the so-called Helmholtz plane. In Figure 5, it is observed that the mean electrostatic potential at the Helmholtz plane  $\Psi_H$  predicted by the non-linear Poisson-Boltzmann theory displays a qualitative agreement regarding the corresponding primitive model Monte Carlo simulations even at large bare surface charge densities  $\sigma_0$ . The same occurs with the capacitive compactness, which displays a decreasing monotonic behaviour in the presence of a  $1:1$  salt when  $\sigma_0$  augments, whereas a non-monotonic behaviour is observed as a function of  $\sigma_0$  in the presence of  $1:2$  and  $1:3$  electrolytes, according to both Monte Carlo simulations and the theoretical non-linear Poisson-Boltzmann results.

Figure 6 portrays the difference of the mean electrostatic potentials  $\Delta_{1:z}^{1:1}\Psi(x) = \Psi^{1:1}(x) - \Psi^{1:z}(x)$  and the normalised difference of the electric fields  $\Delta_{1:z}^{1:1}E(x)/E_0 = (E^{1:1}(x) - E^{1:z}(x))/E_0$  resulting from Monte Carlo simulations and from the non-linear Poisson-Boltzmann equation, for a planar geometry and for different valences of the multivalent coions  $z = z_+ = 2, 3$ . According to Monte Carlo simulations,  $\Delta_{1:z}^{1:1}\Psi(x)$  displays values that do not tend to zero in the whole space even at large values of  $\sigma_0$ . In the case of the non-linear Poisson-Boltzmann equation,  $\Delta_{1:z}^{1:1}\Psi(x)$  goes to zero in the region bounded by the electrode's surface and the Helmholtz plane. However, the  $\Delta_{1:z}^{1:1}\Psi(x)$  obtained via the non-linear Poisson-Boltzmann description displays a qualitative agreement regarding Monte Carlo simulations beyond the Helmholtz plane. Moreover, Monte Carlo simulations confirm the non-linear Poisson-Boltzmann prediction of the augment of the maxima of  $\Delta_{1:z}^{1:1}\Psi(x)$  as a function of the valence  $z$  of the coions. In the case of the  $\Delta_{1:z}^{1:1}E(x)/E_0$ , the non-linear Poisson-Boltzmann data exhibit the same qualitative behaviour displayed by the Monte Carlo simulations, even though the maxima and minima are less accentuated in the former regarding the latter.

## 5. Concluding remarks

The dominance of counterions in the electrical double layer is a theoretical prescription proposed by Valleau and Torrie almost 40 years ago, which it has been groundlessly

thought to be valid [4–14] beyond the classical non-linear Poisson-Boltzmann theory [3].

In several theoretical and simulation works [15,16,20], our research group has demonstrated that if physico-chemical properties characteristic of charged fluids are taken into account consistently, such as ion correlations or ionic excluded volume effects, the electrical properties of  $z:z$  electrolytes asymmetric in size or  $1:z$  equisized electrolytes do not necessarily converge to those of the symmetric electrolyte, in the limit of an infinite electric field at the colloidal surface and when the properties of counterions are the same. That is, we have previously demonstrated that, beyond the classical non-linear Poisson-Boltzmann theory, the counterions do not necessarily dominate in the electrical double layer, and that the properties of coions matter.

To our best knowledge, according to the non-linear Poisson-Boltzmann picture, the dominance of counterions was assumed to be true in whole space, without proof, in the physical chemistry community. Now, in this study we have explicitly shown, via analytical and numerical calculations, that the electrical properties associated to the surface of a planar electrode next to a  $1:z$  electrolyte, such as the surface mean electrostatic potential  $\Psi_0$  or the capacitive compactness  $\tau_c(\Psi_0, \sigma_0)$ , *exactly fulfil* the Valleau and Torrie's prescription of the dominance of counterions in the non-linear Poisson-Boltzmann theory.

On the other hand, we have also proved that, in general, the counterions do not necessarily dominate in the planar electrical double layer at the level of electrostatic properties such as the local mean electrostatic potential  $\Psi(x)$  and the electric field  $E(x)$  in the whole space, that is, in the limit of an infinite surface charge density we have evinced, via analytical and accurate numerical calculations, that, according to the non-linear Poisson-Boltzmann picture, the  $\Psi(x)$  and  $E(x)$  do not converge uniformly in the whole space to the same value in the presence of  $1:z$  electrolytes, even if the properties of monovalent counterions are the same. These results are consistent with new primitive model Monte Carlo simulation data at large bare surface charge densities. The qualitative agreement displayed by the non-linear Poisson-Boltzmann theory regarding the primitive model Monte Carlo simulations is probably due to the fact that the bulk  $1:z$  electrolyte with monovalent counterions is still in the weak electrostatic coupling regime, despite the increase of the corresponding ionic strength as a function of the valence  $z$  of the multivalent coions, when the properties of counterions are fixed. In the presence of multivalent counterions, interesting phenomena such as charge reversal or charge inversion are expected in the electrical double layer [15–17,20]. In such a scenario, the non-linear Poisson-Boltzmann theory

clearly breaks down and more sophisticated theoretical approaches are required, including density functional theories [25], integral equations [15–17,20] and/or the Modified Poisson-Boltzmann theory [33]. Work along this line of research is currently in progress and it will be published elsewhere.

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## Disclosure statement

No potential conflict of interest was reported by the author(s).

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