Expansion and shrinkage of the electrical double layer in charge-asymmetric electrolytes: A non-linear Poisson-Boltzmann description

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A B S T R A C T

The spatial extension or thickness of the electrical double layer determines many thermodynamic and electrokinetic properties of charged colloids in solution. In the classical Debye-Hückel formalism of point ions, the thickness of the electrical double layer around a spherical macroion or next to an infinite planar electrode can be characterized by the bulk Debye length of the supporting ionic fluid. As a result, that approach neglects, at least, the influence of the colloidal charge on the spatial extension of the ionic cloud. Given that the Debye-Hückel formalism of point ions is valid only in the limit of very weak colloidal charges, in this work we use the non-linear Poisson-Boltzmann equation to study the thickness of the electrical double layer near a positively charged electrode in spherical and planar geometries, in the presence of several binary charge-asymmetric $-1:z_+$ point-ions electrolytes with monovalent counterions and multivalent coions. The properties of counterions are maintained fixed, whereas the properties of coions (such as their valence and concentration) are varied fulfilling the bulk electroneutrality condition. The thickness of the ionic cloud is quantified here via the recently introduced capacitive compactness idea (Phys. Chem. Chem. Phys. 20 (2018) 262). Physically, this length represents essentially the separation distance between two electrodes associated to the corresponding *effective* electrical double layer capacitor, in both planar and spherical geometries. Our numerical calculations show that the capacitive compactness obtained via the non-linear Poisson-Boltzmann equation reduces to the Debye length of the supporting bulk electrolyte at the point of zero charge. In the presence of a charge symmetric $-1:+1$ electrolyte, the capacitive compactness always decreases as a function of the colloidal charge. Contrastingly, the electrical double layer may expand or shrink as a function of the surface charge density, in the presence of multivalent coions, which is confirmed here by primitive model Monte Carlo simulations. This last non-monotonic behaviour of the capacitive compactness for multivalent coions, depending on the colloidal charge, is related to the microscopic behaviour of the local electric field, the mean electrostatic potential, and the net ionic charge per unit volume close to the colloidal surface. At very large colloidal charges, the capacitive compactness of all $-1:z_+$ electrolytes collapses onto a single curve illustrating the dominance of counterions in the non-linear Poisson-Boltzmann theory.

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1. Introduction

The ionic cloud surrounding a charged colloid or surface dissolved in a coulombic fluid is the so-called electrical double layer. The spatial extension or thickness of the electrical double layer plays a crucial role in the thermodynamic and electrokinetic properties

of macroions or charged plates in solution [1-24]. According to the classical Debye-Hückel theory of point ions, the separation distance between the electrodes of an effective electrical double layer capacitor for a $z_-:z_+$ electrolyte (with $z_- = -z_+$) is equal to the Debye length of the supporting bulk electrolyte in planar and spherical geometries [25-27]. As a result, in this theoretical description the spatial location of the centroid of charge [27] associated to the diffuse ionic cloud is independent of the magnitude of the colloidal charge. One major limitation of the Debye-Hückel theory is that it is valid only in the limit of very weakly charged surfaces neutralized

by point-ions electrolytes. At non-weak colloidal charges, one would expect, intuitively, that increasing the charge density of a spherical or a planar electrode should have the effect of always reducing the spatial extension of the electrical double layer. In other words, if the colloidal surface charge density increases one would expect, naively, that the net ionic charge per unit volume profile would be closer to the colloidal surface. In this regard, and instead of the Debye length, we use here the novel concept of capacitive compactness [27] to characterize the location of the centroid of charge of a coulombic fluid for several $-1{:}z_+$ point-ions electrolytes near a positive spherical macroion or next to a positive and infinite planar electrode. The properties of monovalent counterions (anions) are the same in all $-1{:}z_+$ electrolytes, whereas the properties of multivalent coions (cations), such as their valence and concentration, are varied accomplishing the bulk electroneutrality condition. In order to calculate the capacitive compactness –and differently from the classical Debye-Hückel viewpoint– we use here the non-linear Poisson-Boltzmann theory, which should provide sensible results in the presence of medium/highly charged colloids *monovalent counterions* and multivalent coions, as it will be shown below.

Our main objective in this study is to investigate the behaviour of the capacitive compactness of charge-asymmetric point-ions electrolytes as a function of the colloidal charge, in spherical and planar geometries. In particular, at large colloidal charges, our theoretical mean-field calculations show that the capacitive compactness curves of all $-1{:}z_+$ point-ions electrolytes collapse onto a single curve. This behaviour illustrates the mean-field dominance of counterions in the non-linear Poisson-Boltzmann theory [28,29]. In accordance with this prescription, the properties of counterions rule or determine the behaviour of the electrical double layer at large electric fields. On the other hand, our numerical calculations display that the capacitive compactness of a $-1{:}+1$ electrolyte decreases monotonically as a function of the colloidal surface charge density. Contrastingly, the capacitive compactness of a $-1{:}z_+$ electrolyte, with multivalent coions, exhibits a non-monotonic behaviour as a function of the colloidal charge: at low surface charge densities the capacitive compactness increases, whereas at high surface charge densities the capacitive compactness decreases monotonically. The above comportment is associated here to the microscopic behaviour of the local electric field, the mean electrostatic potential, and the net ionic diffuse charge per unit volume near the colloidal surface in spherical and planar geometries.

2. Model and methods

2.1. The non-linear Poisson-Boltzmann description

In this study, we consider a point-ions $-1{:}z_+$ electrolyte either i) surrounding a spherical macroion of radius R_M and valence z_M, or ii) bathing a charged and infinite planar electrode with bare surface charge density σ_0^{wall}. The bare surface charge density of the spherical macroion is denoted by $\sigma_0^{sphere} = (e_0 z_M)/(4\pi R_M^2)$, where e_0 is the protonic charge. In both instances, ions can approach up to a closest approach distance b measured from the colloidal surface. This distance defines the location of the so-called Helmholtz plane, as shown in Fig. 1. The Helmholtz plane was introduced in the past century to prevent the appearance of non-physical concentrations of counterions (higher than the ionic close packing concentration) very near the colloidal surface. In this study, two closest approach distances are considered: $b = 2.125$ and $3.3\,\text{Å}$. In addition, and as a reference, a surface charge density of $0.1\,\text{C/m}^2$ is equivalent to an elementary charge e_0 per 160 square angstroms (or 0.6 elementary charges e_0 per 100 square angstroms) approximately.

The non-linear Poisson-Boltzmann equation can be written in terms of the ionic profiles next to the charged colloid. In turn, the
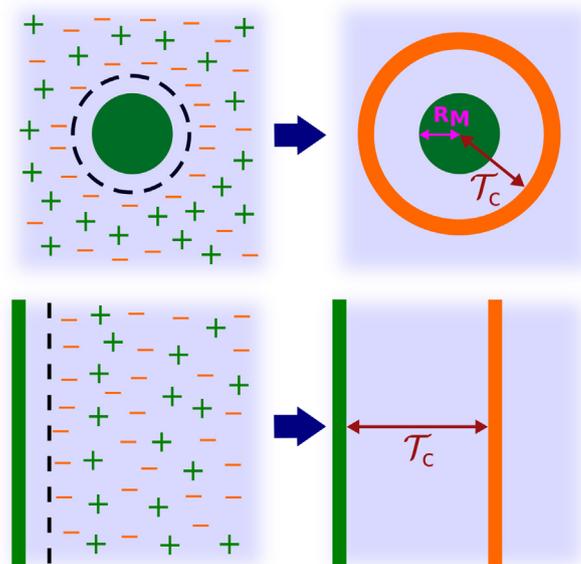
Fig. 1. Effective electrical double layer capacitor in spherical (top) and planar (bottom) geometries. The closest approach distance b between point-ions and the colloidal surface, or Helmholtz plane, is indicated with black dashed lines.

normalized ionic profile $g_i(x)$ of the species i can be formally written, in planar and spherical geometries, in terms of the ionic potential of mean force $W_i(x)$:

$$\rho_i(x) = \rho_i^{bulk} g_i(x) = \rho_i^{bulk} \exp\left(-\frac{W_i(x)}{k_B T}\right), \tag{1}$$

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 colloidal or electrodic surface. 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 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

$$\nabla^2 \psi(x) = -\frac{1}{\varepsilon_0 \epsilon} \sum_i \rho_i^{bulk} z_i e_0 \exp\left(-\frac{e_0 z_i \psi(x)}{k_B T}\right), \tag{2}$$

where ε_0 and ϵ are the vacuum permittivity and the dielectric constant of the solvent, respectively. The linear Poisson-Boltzmann equation can be obtained by linearizing Eq. (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 ψ_0, and the colloidal charge σ_0

$$\psi_0 = \frac{z_M e_0}{4\pi \varepsilon_0 \epsilon R_M (1 + \kappa_D R_M)} \tag{3}$$

in spherical geometry, and

$$\psi_0 = \frac{\sigma_0}{\varepsilon_0 \epsilon \kappa_D} \tag{4}$$

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

$$\kappa_D = \left(\frac{\sum_i \rho_i^{bulk} z_i^2 e_0^2}{\varepsilon_0 \epsilon k_B T} \right)^{\frac{1}{2}}. \tag{5}$$

In the linear Poisson-Boltzmann, or Debye-Hückel theory, the reduced mean electrostatic potential $\psi^*(x) = \psi(x)/\psi_0$ and the reduced electric field $E^*(x) = E(x)/E_0$ have the same functional form in planar geometry, namely

$$\psi^*(x) = E^*(x) = e^{-x/\lambda_D}. \tag{6}$$

In spherical geometry, the reduced mean electrostatic potential $\psi^*(r) = \psi(r)/\psi_0$, and the reduced electric field $E^*(r) = E(r)/E_0$ can be written as

$$\psi^*(r) = \frac{R_M}{r} e^{-(r-R_M)/\lambda_D}, \tag{7}$$

$$E^*(r) = \psi^*(r) \left(\frac{R_M}{r} \right)^2 \left(\frac{r^2 + \lambda_D r}{R_M^2 + \lambda_D R_M} \right), \tag{8}$$

From Eqs. (6)–(8), it is clear that, according to the linear Poisson-Boltzmann or Debye-Hückel theory, the reduced mean electrostatic potential and the reduced electric field (in planar and spherical geometry) are independent of the colloidal surface charge density. This is not necessary the case in the non-linear Poisson-Boltzmann theory, as it will be illustrated below.

On the other hand, if the normalized ionic profiles are known it is possible to write, in general, the integrated charge, the electric field, and the mean electrostatic potential around a spherical macroion of valence z_M as [29]

$$P(r) = z_M + \sum_{i=-,+} \int_0^r z_i \rho_i^{bulk} g_{Mi}(t) 4\pi t^2 dt, \tag{9}$$

$$E^{sphere}(r) = \frac{e_0}{4\pi\varepsilon_0\epsilon} \frac{P(r)}{r^2}, \tag{10}$$

and

$$\psi(r) = -\int_\infty^r E^{sphere}(t)dt = \int_r^\infty E^{sphere}(t)dt. \tag{11}$$

In planar geometry, the global electroneutrality condition implies that the above quantities can be written analogously as [29]

$$\sigma^{wall}(x) = \sigma_0^{wall} + \int_0^x \sum_i \rho_i^{bulk} g_i(t) e_0 z_i dt, \tag{12}$$

$$E^{wall}(x) = \frac{\sigma^{wall}(x)}{\varepsilon_0 \epsilon}, \tag{13}$$

and

$$\psi(x) = \frac{e_0}{\varepsilon_0\epsilon} \int_x^\infty (x-t) \left(\sum_{i=-,+} \rho_i^{bulk} z_i (g_i(t) - 1) \right) dt. \tag{14}$$

In a very recent work [27], some of the present authors have proposed the use of the capacitive compactness τ_c as a novel, accurate and robust measure of the spatial extension of the electrical double layer next to a charged surface. Physically, the capacitive compactness can be thought as the separation distance between two electrodes associated to an effective electrical double layer capacitor,

as shown in Fig. 1. In general, the capacitive compactness in spherical and planar geometries can be written as

$$\tau_c^{sphere} = \left(\frac{1}{R_M} - 4\pi\varepsilon_0\epsilon \frac{\psi_0^{sphere}}{z_M e_0} \right)^{-1} \tag{15}$$

and

$$\tau_c^{wall} = \varepsilon_0 \epsilon \frac{\psi_0^{wall}}{\sigma_0^{wall}}, \tag{16}$$

where ψ_0^{sphere} and ψ_0^{wall} are the mean electrostatic potential at the charged surface in spherical and planar geometries, respectively. Notice that the capacitive compactness in Eq. (15) is measured from the center of the spherical macroion, whereas this quantity is measured from the surface of the planar charged electrode in Eq. (16), as it is shown schematically in Fig. 1.

By substituting Eqs. (3) and (4) in Eqs. (15) and (16), respectively, it is straightforward to obtain the capacitive compactness in the linear Poisson-Boltzmann or Debye-Hückel theory. Following this theoretical description, the capacitive compactness τ_c measured from the colloidal surface is equal to the Debye length in spherical and planar geometries (when the ionic closest approach distance between the point-ions and the colloidal surface is zero). Notice that in this approximation the capacitive compactness τ_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 even at medium/large surface charge densities. The capacitive compactness associated to this higher-order description can be obtained from Eqs. (15) and (16), in spherical and planar geometries, if the mean electrostatic potential is calculated at the colloidal surface in terms the corresponding ionic profiles via Eqs. (11) and (14).

To our best knowledge, there are not exact analytical solutions to the non-linear Poisson-Boltzmann equation in the presence of charge-asymmetric $-1:z_+$ point-ions electrolytes. Thus, numerical solutions of these equations are required. Notice 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 spherical and planar geometries can be found elsewhere [27,28], so we will just briefly sketch them here.

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

$$h_{Mj}(r) = c_{Mj}(r) + \sum_{k=-,+} \rho_k \int h_{Mk}(t) c_{kj}(|\vec{r} - \vec{t}|) dV, \tag{17}$$

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 using the hypernetted-chain (HNC) closure $c_{Mj}(r) = -\beta U_{Mj}(r) + h_{Mj}(r) - ln[h_{Mj}(r) + 1]$ and, 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 used in the integrand of Eq. (17), then the integral equations version of the non-linear Poisson-Boltzmann theory is obtained (see Ref. [28] for the explicit expressions). The integral form of the non-linear Poisson Boltzmann equation for the electrical double layer of a binary electrolyte next to a planar charged surface can be straightforwardly obtained from Eq. (17) by taking the

limit of a colloid with infinite radius [27]. Dropping the subscript M, these equations can be explicitly written as

$$g_i(x) = \exp\left\{-z_i e_0 \beta \psi_0 - z_i\left(\frac{e_0^2}{k_B T \epsilon_0 \epsilon}\right) \int_b^\infty \left[\sum_j z_j \rho_j g_j(t)\right] \mathcal{F}(x,t)\, dt\right\},$$
(18)

for $x \geq b$, $i,j = +,-$, and

$$\mathcal{F}(x,t) = \frac{(x+t) - |x-t|}{2}.$$
(19)

In our finite element implementation, the upper limit in the integral of Eq. (18) was approximated by a cut-off distance $R_{max} = 400\,\text{Å}$, which is at least 130 times larger than the maximum capacitive compactness associated to each $-1{:}z_+$ electrolyte.

2.2. Monte Carlo simulations

In our simulations of the planar electrical double layer, the aqueous electrolyte is modeled using the so-called restricted primitive model. In this representation, the ionic particles are mimicked by *equally-sized* hard spheres of diameter $a = 4.25\,\text{Å}$ with point charges $q_i = z_i e_0$ embedded at their centers. An infinite and impenetrable charged wall is in contact with the ionic particles, which are dissolved in a continuum solvent characterized by a dielectric constant ϵ at a temperature T. The pair interaction potential between any pair of ionic particles is given by

$$U_{ij}(r) = \begin{cases} \infty, & r < a, \\ \frac{z_i z_j e_0^2}{4\pi \varepsilon_0 \epsilon r}, & r \geq a, \end{cases}$$
(20)

where the subscripts $i,j = +,-$; r denotes the distance between the centers of two charged hard particles of type i and j, and ϵ is the dielectric constant in all space, including the interior of the solid electrode.

The interaction potential between a hard ionic particle of type i and the infinite and impenetrable charged electrode is given by

$$U_i^{wall}(x) = \begin{cases} \infty, & x < \frac{a}{2}, \\ -\frac{\sigma_0 z_i e_0}{\varepsilon_0 \epsilon}|x|, & \text{if } x \geq \frac{a}{2}, \end{cases}$$
(21)

where σ_0 is the surface charge density on the electrode's surface. The electrode's surface is placed at $x = 0$, and the closest approach distance between the ionic particles of diameter a and the hard electrode is located at $b = (a/2)$, which defines the so-called Helmholtz plane. Monte Carlo (MC) simulations of an aqueous electrolyte in the presence of a charged electrode were performed in the canonical *NVT* ensemble. A rectangular simulation cell of volume $V = W^2 L$ was considered. Periodic boundary conditions were used in two directions (y- and z-axis), and a finite length along the x-axis was considered. Two infinite and impenetrable walls in both sides of the simulation cell were used to confine the electrolyte. One wall was charged with a surface charge density σ_0 and the other one was neutral. The width and transversal section of the simulation cell were $W = 126.57\,\text{Å}$ and W^2, respectively. The length L of the simulation cell was at least two times the width W, and it was adjusted to reach the desired bulk concentration with an error of 1% or less. According to this prescription, notice that the length L is at least 80 times the maximum capacitive compactness associated to each $-1{:}z_+$ electrolyte. In a typical run of a $-1{:}{+}1$ salt, at a concentration 1 M and electrode's surface charge density $\sigma_0 = 0.05\,\text{C/m}^2$, approximately

4800 ions were placed inside the simulation box. In all simulations, the surface charge density on the electrode was neutralized by the presence of an excess of monovalent counterions. The classical Metropolis algorithm was used in the *NVT* canonical simulations. At least 1×10^5 MC cycles were performed in the thermalization process, and 1×10^6 MC cycles were done in the production runs. The electrostatic interactions were calculated via the charged-sheets method proposed by Torrie and Valleau [30] using Boda's modification [31], in which an infinite charged plane with a square hole is considered in the simulation cell. More details about the Monte Carlo simulations can be consulted elsewhere [29,32-34]. The ionic profiles were quantified via singlet distribution functions $g_i(x)$ for each ionic species $i = +,-$. Once these ionic profiles were known, the capacitive compactness was calculated by using Eqs. (14) and (16) in planar geometry.
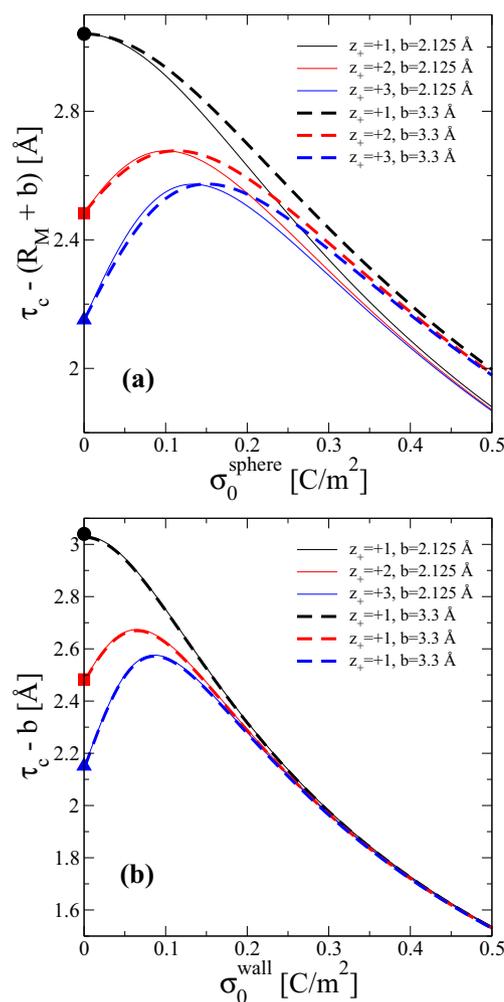
Fig. 2. Capacitive compactness τ_c calculated via the non-linear Poisson-Boltzmann theory (a) in the presence of a spherical macroion of radius $R_M = 15\,\text{Å}$ and bare surface charge density σ_0^{sphere}, and (b) in the presence of an infinite charged hard wall with bare surface charge density σ_0^{wall}. In both cases, the charged colloid is in contact with a binary charge-asymmetric $-1{:}z_+$ point-ions electrolyte with an ionic closest approach distance b to the colloidal surface for both ionic species. The concentration of anions is $\rho_- = 1\,\text{M}$ in all cases, and the ionic strength of the solution is 1, 1.5 and 2 M, for $z_+ = +1$, $z_+ = +2$, and $z_+ = +3$, respectively. τ_c is measured from the center of the macroion in spherical geometry, and from the electrode's surface in planar geometry. Filled black circles, red squares, and blue triangles at the point of zero charge (uncharged colloid) correspond to the bulk Debye length of the supporting electrolyte for $z_+ = +1$, $z_+ = +2$, and $z_+ = +3$, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

The behaviour of the capacitive compactness τ_c associated to a charge-asymmetric sizeless electrolyte either surrounding a positive spherical macroion or next to a positive planar hard wall is displayed in Fig. 2 (a) and (b), respectively. In both figures, the ionic concentration and the valence of counterions (anions) are 1 M and $z_- = -1$, respectively. Two different closest approach distances between point ions and the colloidal surface, or Helmholtz planes, are considered: $b = 2.125$ Å, and $b = 3.3$ Å for a binary electrolyte. For a given Helmholtz plane, three valences $z_+ = +1, +2, +3$ are considered for coions (cations), whose concentration is adjusted to fulfill the bulk electroneutrality condition $z_-\rho_-^{bulk} + z_+\rho_+^{bulk} = 0$. In both geometries (spherical and planar), it is observed that the capacitive compactness measured from the Helmholtz plane tends asymptotically to the Debye length of the supporting bulk electrolyte (indicated by filled symbols) very close to the point of zero charge (i.e., when the surface of the spherical macroion or the planar electrode is uncharged). This limit capacitive compactness is predicted by the linearized Poisson-Boltzmann theory in the presence of point-ions electrolytes. According to this last theoretical formalism, τ_c is independent of the colloidal charge and only depends on those properties of the supporting bulk electrolyte defining the Debye length, such as the valence and concentration of ions, as well as the temperature and dielectric permittivity of the solvent. On the contrary, in the non-linear Poisson-Boltzmann theory τ_c depends on the colloidal charge, the electrode's geometry, and the properties of the electrolyte defining the bulk Debye length. When the colloidal charge increases, the behaviour of τ_c is very different depending if coions are monovalent or multivalent. In the presence of monovalent coions, τ_c decreases monotonically when the colloidal charge increases, as shown in Fig. 2. Thus, the separation distance between the electrodes of the associated effective capacitor, in both geometries, decreases and the electrical double layer becomes more compact. *Contrastingly, τ_c displays a non-monotonic behaviour when coions are multivalent.* In specific, at very low colloidal charges the capacitive compactness with multivalent coions increases until the surface charge density reaches a critical value $\sigma_0^{critical}$ at which τ_c displays a maximum. When the colloidal charge further increases, τ_c decreases as a function of the surface charge density. In other words, the separation
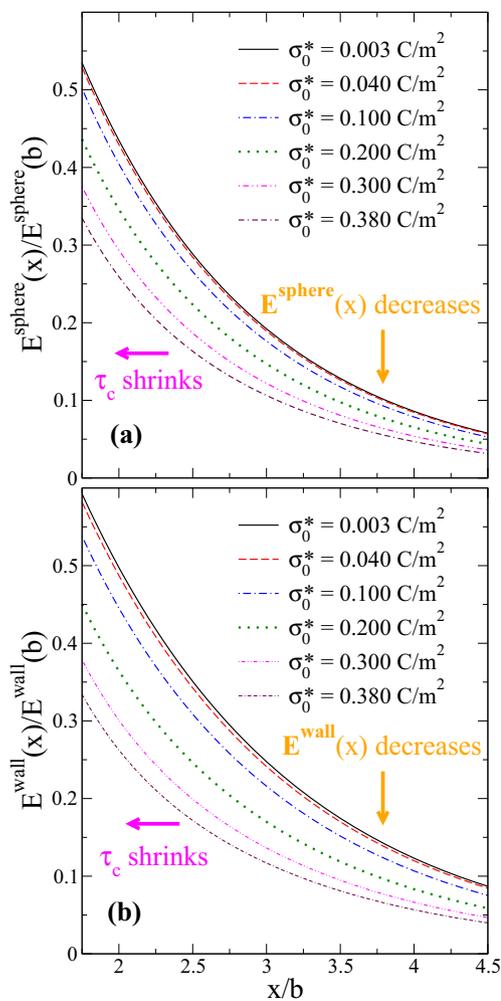
Fig. 4. Electric field obtained via the non-linear Poisson-Boltzmann theory (a) around a spherical macroion of radius $R_M = 15$ Å and bare surface charge density σ_0^{sphere}, and (b) next to an infinite charged hard wall with bare surface charge density σ_0^{wall}, for several colloidal charges. In both cases, the charged colloid is in contact with a binary charge-symmetric -1:$+1$ point-ions electrolyte with an ionic closest approach distance $b = 2.125$ Å to the colloidal surface for both ionic species. The concentration of anions is $\rho_- = 1$ M and the ionic strength of the solution is 1 M in all instances. For the spherical macroion, the effective surface charge density is $\sigma_0^* = (R_M/(R_M + b))^2\sigma_0^{sphere}$. For the infinite planar wall, the effective surface charge density is $\sigma_0^* = \sigma_0^{wall}$. The distance x is measured from the colloidal surface in both cases.

distance between the electrodes of the associated effective capacitor increases and decreases depending on the magnitude of the colloidal surface charge. This behaviour indicates *an expansion and a shrinkage of the electrical double layer that depends on the geometry and charge of the colloid in the presence of multivalent coions.*

Another interesting feature observed in Fig. 2 is that the τ_c curves, associated to electrolytes with the same Helmholtz plane and different coions, converge and collapse onto a single curve at large colloidal charges when the properties of counterions are the same in all instances. Such a behaviour illustrates the so-called dominance of counterions in the non-linear Poisson-Boltzmann theory [28]. This mean-field formalism predicts that two binary electrolytes, in which the counterions have the same properties (differing only in the properties of coions), will display the same microscopic and thermodynamic properties at very large colloidal charges. In other words, at large electric fields, the properties of counterions rule or determine the structure of the electrical double layer and the characteristics

Fig. 3. The same as in Fig. 2 (a) but for an effective surface charge density $\sigma_0^* = (R_M/(R_M + b))^2\sigma_0^{sphere}$, where σ_0^{sphere} is the bare charge density on the surface of the spherical macroion.
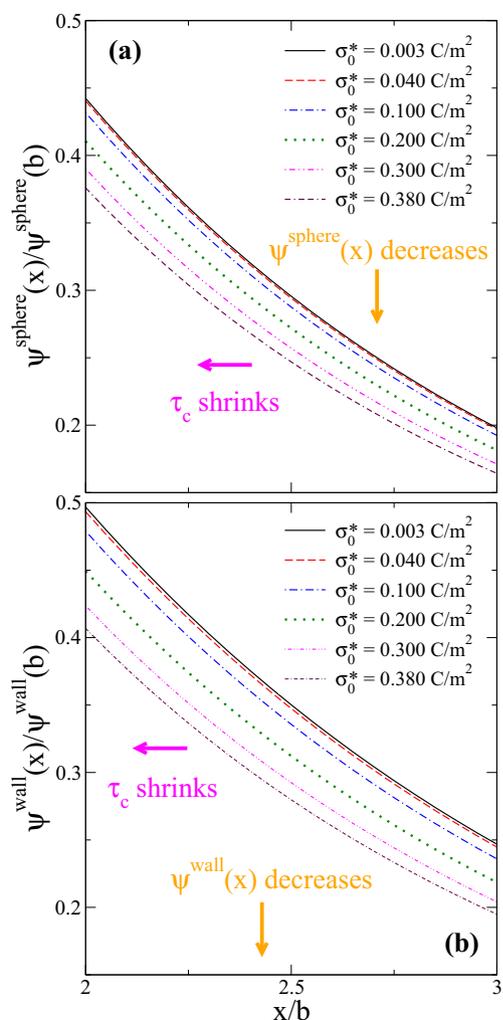
Fig. 5. Mean electrostatic potential obtained via the non-linear Poisson-Boltzmann theory (a) around a spherical macroion of radius $R_M = 15$ Å and bare surface charge density σ_0^{sphere}, and (b) next to an infinite charged hard wall with bare surface charge density σ_0^{wall}, for several colloidal charges. In both cases, the charged colloid is in contact with a binary charge-symmetric -1:$+1$ point-ions electrolyte with an ionic closest approach distance $b = 2.125$ Å to the colloidal surface for both ionic species. The concentration of anions is $\rho_- = 1$ M and the ionic strength of the solution is 1 M in all instances. For the spherical macroion, the effective surface charge density is $\sigma_0^* = (R_M/(R_M + b))^2 \sigma_0^{sphere}$. For the infinite planar wall, the effective surface charge density is $\sigma_0^* = \sigma_0^{wall}$. The distance x is measured from the colloidal surface in both cases.

Fig. 6. The same as in Fig. 4 but for a binary charge-asymmetric -1:$+3$ point-ions electrolyte with an ionic closest approach distance $b = 2.125$ Å to the colloidal surface for both ionic species. The concentration of anions is $\rho_- = 1$ M and the ionic strength of the solution is 2 M in all instances. The distance x is measured from the colloidal surface in both cases.

of coions become irrelevant. In spherical geometry, the asymptotic value of τ_c at large colloidal charges depends on b, as shown in Fig. 2 (a). In planar geometry, the asymptotic value of τ_c is the same independently of the value of b when τ_c is measured from the closest approach distance between the point-ions and the planar electrode, as portrayed in Fig. 2 (b). In addition, note that the capacitive compactness curves displayed in Fig. 2 (a), corresponding to the same -1:$+z$ electrolyte for two different Helmholtz planes, can merge onto the same curve if τ_c is plotted as a function of an effective surface charge density $\sigma_0^* = (R_M/(R_M + b))^2 \sigma_0^{sphere}$, as shown in Fig. 3 (notice that for a plate $\sigma_0^* = \sigma_0^{wall}$). Another notable trait discerned in Figs. 2 (b) and 3 is that the onset of the asymptotic collapse of the τ_c curves onto a single curve occurs at lower values of the effective surface charge density in planar geometry regarding the spherical geometry. This geometric effect is due to the fact that the electric field near an infinite planar electrode is stronger than the electric

field associated to an spherical colloid with the same effective surface charge density.

The behaviour of the capacitive compactness τ_c can be associated to the microscopic structure of the electrical double layer. In quantitative terms, this feature will be discussed below in terms of the local electric field, the mean electrostatic potential, and the net charge per unit volume near the colloidal surface. With this purpose in mind, the behaviour of the electric field and the mean electrostatic potential in the presence of a -1:$+1$ electrolyte as a function of the distance to the colloidal surface is plotted in Figs. 4 and 5, respectively, in spherical and planar geometries. In both figures, it is observed that the electric field and the mean electrostatic potential deswells or becomes more compact when the colloidal surface charge density increases in each geometry, that is, $E(x, \sigma_0^*)/E(b, \sigma_0^*) < E(x, \sigma_0^{*'})/E(b, \sigma_0^{*'})$ and $\psi(x, \sigma_0^*)/\psi(b, \sigma_0^*) < \psi(x, \sigma_0^{*'})/\psi(b, \sigma_0^{*'})$ if $\sigma_0^* > \sigma_0^{*'}$ for all x displayed, where x is the perpendicular distance between a point in the three-dimensional space and the colloidal surface, in spherical and planar geometries. As a result, the electrical double layer shrinks monotonically when the colloidal charge increases in charge-symmetric monovalent electrolytes. Such a behaviour, as a function of the magnitude of the surface charge density, contrasts with that
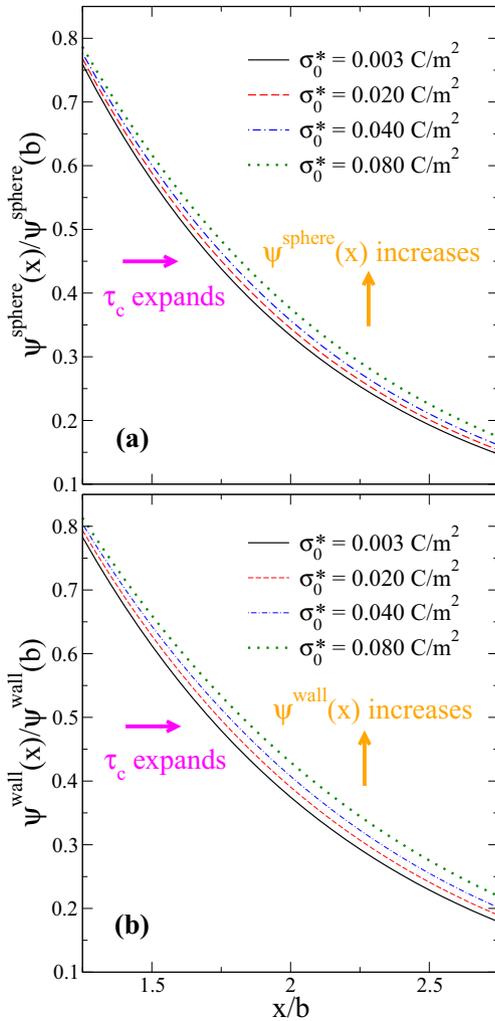
Fig. 7. The same as in Fig. 5 but for a binary charge-asymmetric $-1{:}+3$ point-ions electrolyte with an ionic closest approach distance $b = 2.125\,\text{Å}$ to the colloidal surface for both ionic species. The concentration of anions is $\rho_- = 1\,\text{M}$ and the ionic strength of the solution is $2\,\text{M}$ in all instances. The distance x is measured from the colloidal surface in both cases.

Fig. 8. The same as in Fig. 6 but for high colloidal charges.

observed in the presence of an electrolyte constituted by monovalent counterions, and divalent or trivalent coions. In particular, the electric field and the mean electrostatic potential in the presence of trivalent coions as a function of the distance to the colloidal surface is plotted in Figs. 6 and 7, respectively, for several low surface charge densities in spherical and planar geometries. In both figures, an opposite behaviour to that displayed in Figs. 4 and 5 is observed, that is, in this instance the electric field and the mean electrostatic potential swells or dilates when the surface charge density increases, that is, $E(x, \sigma_0^*)/E(b, \sigma_0^*) > E(x, \sigma_0^{*\prime})/E(b, \sigma_0^{*\prime})$ and $\psi(x, \sigma_0^*)/\psi(b, \sigma_0^*) > \psi(x, \sigma_0^{*\prime})/\psi(b, \sigma_0^{*\prime})$ if $\sigma_0^* > \sigma_0^{*\prime}$ for all x displayed. Thus, the electrical double layer expands at low surface charge densities when the colloidal charge increases in the presence of trivalent coions. The electric field and the mean electrostatic potential as a function of the distance to the colloidal surface is plotted in Figs. 8 and 9, respectively, now at large colloidal charges in spherical and planar geometries. In both figures, an analogous behaviour to that displayed in Figs. 4 and 5 is seen, viz., for highly electrified surfaces, the local electric field and the mean electrostatic potential associated to a $-1{:}+3$ electrolyte deswells or becomes more compact when the surface charge density increases. In other words, the electrical double layer associated to monovalent counterions and trivalent coions

shrinks at large colloidal charges, as occurred in the presence of a $-1{:}+1$ monovalent salt, in planar and spherical geometries. In summary, the microscopic behaviour of the local electric field and the mean electrostatic potential displayed above is totally consistent with the behaviour of the capacitive compactness displayed in Fig. 2, namely if the electric field or the mean electrostatic potential expands or swells as a function of the colloidal charge then the magnitude of the capacitive compactness increases; on the contrary, if the electric field or the mean electrostatic potential shrinks or deswells as a function of the colloidal charge then magnitude of the capacitive compactness decreases.

The spatial extension of the electrical double layer can be also analyzed in terms of the net ionic charge per unit volume $\rho_{el}(\vec{r}) = \sum_i z_i e_0 \rho_i(\vec{r})$, for $i = +, -$. In planar geometry, this quantity is proportional to the difference between the singlets of counterions (anions) and coions (cations). Then, we define $g_{diff}^*(x)$ as the difference between these ionic singlets normalized regarding the value of such a difference at the ionic closest approach distance, or Helmholtz plane:

$$g_{diff}^*(x) = \frac{g_-^{wall}(x) - g_+^{wall}(x)}{g_-^{wall}(b) - g_+^{wall}(b)}. \tag{22}$$

The behaviour of $g_{diff}^*(x)$, associated to the local electric field displayed in Fig. 4 (b) for a $-1{:}+1$ electrolyte in planar geometry, is
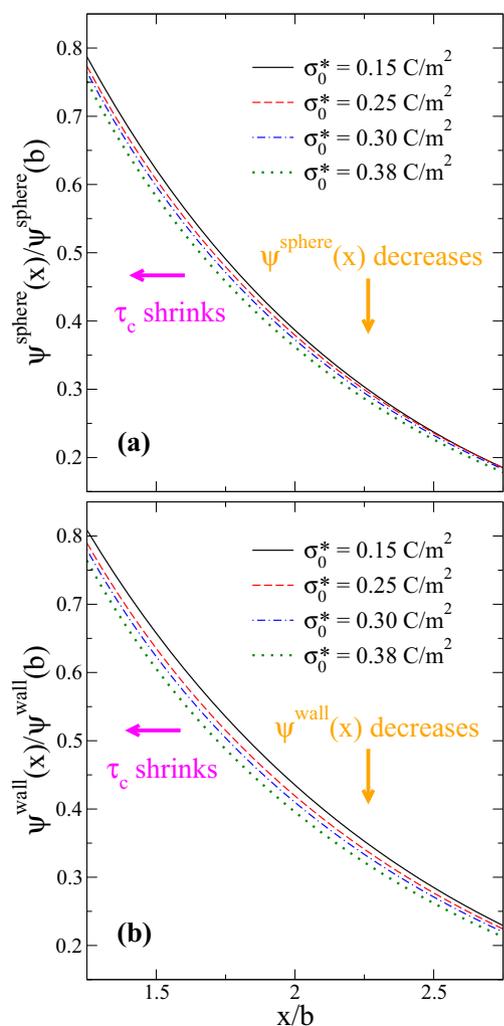
Fig. 9. The same as in Fig. 7 but for high colloidal charges.

Fig. 10. Normalized difference between the ionic singlets $g_-(x)$ and $g_+(x)$ next to an infinite charged hard wall with bare surface charge density σ_0^{wall}. The ionic singlet difference $g_{diff}^*(x) = [g_-(x) - g_+(x)]/[g_-(b) - g_+(b)]$ has been obtained via the non-linear Poisson-Boltzmann theory in planar geometry. The infinite charged hard wall is in contact with a binary charge-symmetric -1:$+1$ point-ions electrolyte with an ionic closest approach distance $b = 2.125$ Å to the colloidal surface. The ionic concentration of anions is $\rho_- = 1$ M and the ionic strength of the solution is 1 M in all cases. The effective surface charge density is $\sigma_0^* = \sigma_0^{wall}$. The distance x is measured from the colloidal surface.

presented in Fig. 10. Here, it is observed that $g_{diff}^*(x)$ approaches to the colloidal surface monotonically when the surface charge density increases, that is, $g_{diff}^*(x,\sigma_0^*) < g_{diff}^*(x,\sigma_0^{*\prime})$ if $\sigma_0^* > \sigma_0^{*\prime}$ for all x. As a result, the electrical double layer deswells or becomes more compact monotonically as a function of the colloidal charge. This microscopic behaviour is consistent with the shrinking of the local electric field observed in Fig. 4 (b) and the deswelling of τ_c displayed in Fig. 2 (b). On the other hand, Fig. 11 portrays the behaviour of the $g_{diff}^*(x)$ associated to a -1:$+3$ electrolyte in planar geometry for several colloidal charges. In particular, note that the $g_{diff}^*(x)$ plotted in Fig. 11 (a) and (b) corresponds to the local electric field displayed in Figs. 6 (b) and 8(b), respectively. At low colloidal charges, $g_{diff}^*(x)$ goes far away from the colloidal surface when the surface charge density increases, that is, $g_{diff}^*(x,\sigma_0^*) > g_{diff}^*(x,\sigma_0^{*\prime})$ if $\sigma_0^* > \sigma_0^{*\prime}$ for all x. Thus, the electrical double layer swells or expands when the colloidal charge augments in the presence of trivalent coions. This microscopic behaviour is also consistent with the expansion of the local electric field seen in Fig. 6 (b) and the swelling of τ_c observed in Fig. 2 (b) at low the surface charge densities. Contrastingly, at high colloidal charges, the $g_{diff}^*(x)$ curves displayed in Fig. 11 (b) show an analogous behaviour to that observed in the presence of monovalent coions (see Fig. 10), that is, $g_{diff}^*(x,\sigma_0^*) < g_{diff}^*(x,\sigma_0^{*\prime})$ if $\sigma_0^* > \sigma_0^{*\prime}$ for all x. As a result, at large surface charge densities, the electrical double layer becomes more compact when the colloidal charge increases in the presence of trivalent coions.

The effect of the geometry in the value of the capacitive compactness τ_c is shown in Fig. 12. Notice that $\tau_c^* = \tau_c - b$ and $\tau_c^* = \tau_c - (R_M + b)$ in planar and spherical geometries, respectively. In particular, in Fig. 12 (a) it is observed that the separation distance between the two electrodes associated to the effective electrical double layer capacitor decreases faster in planar geometry regarding the spherical geometry, that is, $\tau_c^{*,wall}(\sigma_0^*) < \tau_c^{*,sphere}(\sigma_0^*)$ for all σ_0^* in -1:$+1$ electrolytes. In the presence of -1:z_+ electrolytes, with multivalent coions, two regimes can be observed in Fig. 12 (b) and (c): in the first regime $\tau_c^{*,wall}(\sigma_0^*) > \tau_c^{*,sphere}(\sigma_0^*)$ if $\sigma_0^* < \sigma_0^{*\prime\prime}$, whereas the opposite behaviour is observed if $\sigma_0^* > \sigma_0^{*\prime\prime}$, that is, in the second regime $\tau_c^{*,wall}(\sigma_0^*) < \tau_c^{*,sphere}(\sigma_0^*)$.

On the other hand, the influence of the ionic strength in the magnitude of the capacitive compactness τ_c is shown in Fig. 13. In this figure, it is remarkable that the difference between the capacitive compactness at the point of zero charge and the maximum capacitive compactness associated to multivalent coions *increases* when the ionic strength of the binary electrolyte *decreases*.

As a final and very important point, in order to demonstrate that the expansion/shrinkage of the electrical double layer discussed above is not just an artifact of the non-linear Poisson-Boltzmann theory, Fig. 14 presents a comparison with Monte Carlo simulations. Here, it is observed that simulations confirm the main predictions of the non-linear Poisson-Boltzmann equation, namely i) the monotonic decreasing of the capacitive compactness in the presence of a -1:$+1$ electrolyte next to a planar electrode as a function of the surface charge density; and ii) the non-monotonic behaviour of the capacitive compactness in the presence of multivalent coions as a function of the colloidal charge.

4. Concluding remarks

The classical and more widely used parameter to determine the thickness of the electrical double layer around a spherical macroion or next to a charged plate is the Debye length of the supporting ionic fluid in bulk. This prescription arises naturally from the
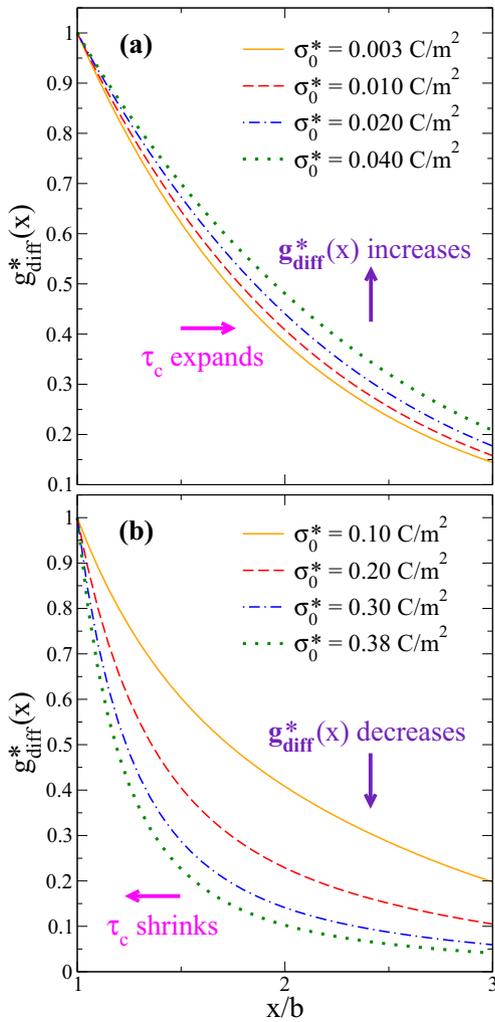
Fig. 11. Normalized difference between the ionic singlets $g_-(x)$ and $g_+(x)$ next to an infinite charged hard wall with bare surface charge density σ_0^{wall}. The ionic singlet difference $g_{diff}^*(x) = [g_-^{wall}(x) - g_+^{wall}(x)]/[g_-^{wall}(b) - g_+^{wall}(b)]$ has been obtained via the non-linear Poisson-Boltzmann theory in planar geometry. The infinite charged hard wall is in contact with a binary charge-asymmetric $-1{:}+3$ point-ions electrolyte with an ionic closest approach distance $b = 2.125$ Å to the colloidal surface. The ionic concentration of anions is $\rho_- = 1$ M and the ionic strength of the solution is 2 M in all cases. The effective surface charge density is $\sigma_0^* = \sigma_0^{wall}$. The distance x is measured from the colloidal surface.

Fig. 12. Capacitive compactness measured from the Helmholtz plane τ_c^* as a function of the effective surface charge density σ_0^*. Notice that $\tau_c^* = \tau_c - b$ and $\tau_c^* = \tau_c - (R_M + b)$ in planar and spherical geometries, respectively. The colloid can be a small spherical macroion with radius $R_M = 15$ Å or an infinite planar charged wall in the presence of a binary charge-asymmetric $-1{:}+z$ point-ions electrolyte, with an ionic closest approach distance $b = 2.125$ Å to the colloidal surface in all instances. In the spherical case, the macroion has a bare surface charge density σ_0^{sphere}, and an effective surface charge density $\sigma_0^* = (R_M/(R_M + b))^2\sigma_0^{sphere}$. In the planar instance $\sigma_0^* = \sigma_0^{wall}$, where σ_0^{wall} is the bare charge density on the electrode's surface. The concentration of anions is $\rho_- = 1$ M in all cases, and the ionic strength of the solution is 1, 1.5 and 2 M, for $z_+ = +1$, $z_+ = +2$, and $z_+ = +3$, respectively. The filled black circle, the red square, and the blue triangle at the point of zero charge (uncharged colloid) correspond to the bulk Debye length of the supporting electrolyte for $z_+ = +1$, $z_+ = +2$, and $z_+ = +3$, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

linear Poisson-Boltzmann or Debye-Hückel theory of point-ions electrolytes. In a very recent work [27], we have proposed the general concept of capacitive compactness to quantify the thickness of the electrical double layer in spherical and planar geometries. The statistical mechanics definition of the capacitive compactness, derived from classical electromagnetism principles, supports its robustness as a general concept, allowing to include many physical effects characteristic of coulombic fluids such as the colloidal charge, ion correlations, ionic excluded volume effects, image charges, and van der Waals attractions. From a microscopic point of view, the idea of capacitive compactness is limited only by the mathematical model used to describe a charged fluid, and by the accuracy of the theory or simulations used to calculate the ionic profiles that neutralize a charged colloid. Physically, the capacitive compactness can be essentially defined as the separation distance between two electrodes associated to an effective electrical double layer capacitor, when the voltage between the effective electrodes is the mean electrostatic potential on the colloidal surface (measured with respect to its value at the bulk of the supporting ionic fluid) [27]. In one of the most

simple theoretical descriptions of coulombic fluids, namely the linear Poisson-Boltzmann or Debye-Hückel theory of point ions, the capacitive compactness is independent of the colloidal charge and reduces to the bulk Debye length of the bathing ionic fluid in spherical and planar geometries. A more realistic scenario could include the effect of the colloidal surface charge density in the spatial extension, or thickness, of the electrical double layer. With this purpose in mind, we have used here the non-linear Poisson-Boltzmann equation to study the capacitive compactness of several $-1{:}z_+$ point-ions electrolytes. In these electrical double layer systems, the properties of monovalent counterions (anions) have been maintained fixed, whereas the properties of multivalent coions (cations), such as their valence and ionic concentration, have been varied but fulfilling the bulk electroneutrality condition. At large colloidal charges, we
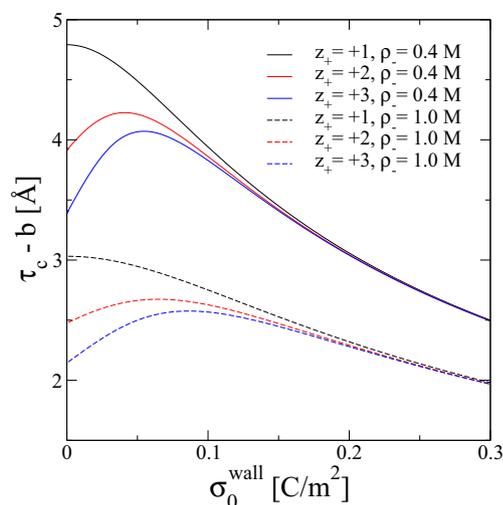
Fig. 13. Effect of the ionic strength on the capacitive compactness τ_c associated to a binary charge-asymmetric $-1{:}+z$ point-ions electrolyte, according to the non-linear Poisson-Boltzmann theory, in the presence of an infinite planar charged wall. In all instances, the ionic closest approach distance to the colloidal surface is $b = 2.125\,\text{Å}$. σ_0^{wall} is the bare charge density on the electrode's surface. The concentration of anions (counterions) is $\rho_- = 0.4\,\text{M}$ for solid lines and $\rho_- = 1\,\text{M}$ for dashed lines. The concentration of cations (coions) is ρ_-/z_+ for solid and dashed lines.

have demonstrated the non-linear Poisson-Boltzmann dominance of counterions in terms of the capacitive compactness, when multivalent coions and monovalent counterions are present in spherical and planar geometries. According to this prescription, the properties of counterions rule or determine the characteristics of the electrical double layer at large colloidal charges. In other words, in the presence of large electric fields, the microscopic and macroscopic properties of $-1{:}z_+$ charge-asymmetric electrolytes converge to the same values if the properties of the monovalent counterions are the same. Thus, the properties of coions are irrelevant at large colloidal charges in the non-linear Poisson-Boltzmann picture of point-ions.

The capacitive compactness concept has been used very recently to characterize the thickness of a charge asymmetric $-2{:}+1$ model molten salt in the presence of an infinite and impenetrable positively charged electrode [27]. In that study, simulation and integral equations calculations including ion correlations and ionic excluded volume effects evidenced that the capacitive compactness as a function of the colloidal charge i) can decrease asymmetrically at low ionic concentrations depending on the sign of the colloid, ii) can reach a limit value, becoming "arrested", in the presence of divalent counterions at high ionic concentrations, and iii) can "expand" in the presence of monovalent counterions at high ionic concentrations. A very interesting feature of the present study is the observation that *a very simple mean field approach, such as the non-linear Poisson-Boltzmann theory, is able to predict a non-monotonic behaviour (expansion and shrinkage) of the electrical double layer even in the absence of ion correlations and ionic excluded volume effects.* Specifically, we have shown here that the capacitive compactness decreases monotonically, in the presence of $-1{:}+1$ monovalent electrolytes, as a function of the colloidal charge for a wide range of surface charge densities. Notwithstanding, in the presence of $-1{:}z_+$ electrolytes, with monovalent counterions and multivalent coions, the capacitive compactness displays a non-monotonic behaviour as a function of the colloidal charge. At low colloidal charges, the capacitive compactness expands or swells reaching a maximum value at some critical surface charge density. When the surface charge density further increases, the capacitive compactness shrinks or deswell displaying the same monotonic trend displayed by the $-1{:}+1$ electrolyte. Relevantly, this phenomenology has been confirmed here by
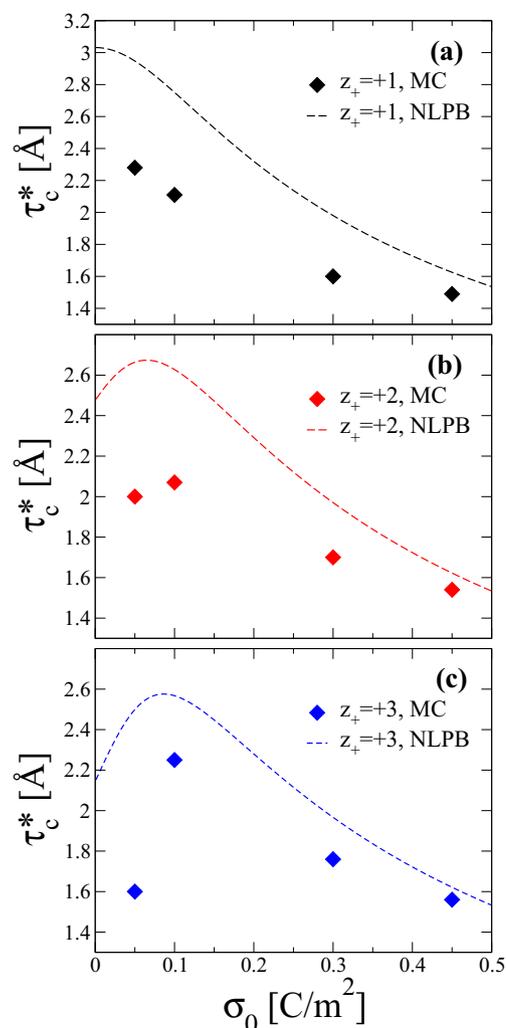
Fig. 14. Monte Carlo simulations of the capacitive compactness τ_c associated to a binary charge-asymmetric $-1{:}+z$ point-ions electrolyte in the presence of an infinite planar charged wall. In all instances, the ionic closest approach distance to the colloidal surface is $b = 2.125\,\text{Å}$. σ_0^{wall} is the bare charge density on the electrode's surface. The concentration of anions (counterions) is $\rho_- = 1\,\text{M}$ and the concentration of cations (coions) is ρ_-/z_+ in all cases. Solid symbols correspond to Monte Carlo simulations, and dashed lines are associated to theoretical predictions of the non-linear Poisson-Boltzmann equation.

Monte Carlo simulations of charge-asymmetric electrolytes in the primitive model.

On the other hand, in this study the behaviour of the capacitive compactness has been also connected to the microscopic structure of the electrical double layer via the local electric field, the mean electrostatic potential, and the net ionic charge per unit volume. Moreover, we have shown that an expansion or swelling of these three quantities, as a function of colloidal charge, can be associated to an increase in the magnitude of the capacitive compactness. On the contrary, when the local electric field, the mean electrostatic potential, and the net ionic charge per unit volume shrink or deswell, the magnitude of the capacitive compactness decreases. The role of the geometry in the behaviour of the capacitive compactness has been also investigated as a function of the colloidal charge. In this regard, the capacitive compactness decreases faster in planar geometry regarding the spherical geometry as a function of the effective bare surface charge density in the presence of monovalent $-1{:}+1$ charge-symmetric sizeless ions. Contrastingly, two regimes can be observed in the presence of multivalent coions. In the first regime, at

low surface charge densities, the capacitive compactness as a function of the reduced bare surface charge density increases faster in planar geometry compared to the spherical geometry. In the second regime, at large surface charge densities, τ_c decreases more rapidly for a plane than for a colloidal sphere. The expansion and a shrinkage of the electrical double layer reported here, in the presence of multivalent coions, is very interesting considering that *this effect arises even in the presence of point-ions in a very simple mean-field approach*. A more realistic model could include other physical features typical of charged fluids, such as ion correlations, ionic excluded volume effects, image charges, and van der Waals short-range attractions. Work along those directions, in order to analyze the corresponding capacitive compactness, is currently in progress and will be published elsewhere.

Acknowledgments

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