On the regimes of charge reversal

Felipe Jiménez-Ángeles and Marcelo Lozada-Cassou
Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, Lázaro Cárdenas 152, 07730 México, D. F., México

(Dated: November 17, 2018)

Charge reversal of the planar electrical double layer is studied by means of a well known integral equations theory. By a numerical analysis, a diagram is constructed with the onset points of charge reversal in the space of the fundamental variables of the system. Within this diagram two regimes of charge reversal are identified, referred to as oscillatory and non oscillatory. We found that these two regimes can be distinguished through a simple formula. Furthermore, a symmetry between electrostatic and size correlations in charge reversal is exhibited. The agreement of our results with other theories and molecular simulations data is discussed.

PACS numbers:

I. INTRODUCTION

Charged particles are naturally adsorbed onto an oppositely charged surface, however, temperature prevents them to completely condensate producing a diffuse ionic concentration profile known as the electrical double layer (EDL). Intuitively one might expect that the adsorbed counterions in the EDL are just the necessary to compensate the surface’s charge, however, for certain conditions, they overcompensate it producing a surface charge inversion. Hence, an inversion of the local electric field takes place next to the first counterions layer and, consequently, coions are attracted to form a second layer referred to as charge inversion of the EDL.

Charge reversal (CR) and charge inversion (CI) have motivated a large number of studies in the past \[1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15\]. These effects have been observed in the formation of self-assembled polyelectrolyte layers on a charged substrate \[16\], self-assembled DNA-lipid membrane complexes \[17\] and anomalous macroions adsorption on Langmuir films \[18\]. Furthermore, CR has been associated with reverse of the electrophoretic mobility of charged colloids \[19, 20, 21, 22\] and polyelectrolytes \[22\] as well as with attraction between like charged macroparticles \[24, 25, 26\] and DNA condensation \[27\].

CR and CI manifest as alternated layers of coions and counterions in the neighborhood of a charged interface, i.e., imply spatial oscillations of the inhomogeneous charge distribution profiles. For bulk electrolytes, the oscillatory behavior of the pair correlation functions was predicted by Stillinger and Lovett \[28\] as a consequence of their second moment condition. The oscillations of the inhomogeneous charge density profiles have been observed in studies where the restricted primitive model (RPM) electrolyte is used to model the diffuse EDL \[12, 29, 30, 31, 32, 33, 34, 35\]. For the EDL produced by a RPM electrolyte at a planar interface, two regimes of CR have been distinguished \[34, 35\], i.e., (i) the oscillatory and (ii) non oscillatory. These regimes are named according to the behavior of the electrolyte pair correlation functions in bulk. In the former regime, since the bulk pair correlation functions oscillate, any disturbance caused by an external electric field is propagated in the same way, therefore, CR occurs for any nonzero surface charge density. In the second regime, a sufficiently high surface charge density is necessary to produce CR. In both regimes, short range and long range correlations play an important role in the surface CR \[4, 15\].

For some cases, the onset points of oscillations of the bulk ionic pair correlation functions \[36\] and EDL-CR \[4, 6, 37\] have been computed, however, a complete picture of both phenomena and their interrelationship is still missing. To fill this void, we construct a CR diagram for the planar EDL in terms of its fundamental variables, i.e., the particles volume fraction (\(\eta\)), the ion-ion (\(\zeta\)) and ion-wall (\(\gamma\)) Coulomb coupling. We also analyze the dependence of CR on each variable. Hence, the reminder of the paper is organized as follows: in section II we describe the model and theory. Section III contains the results and their discussion, and, finally, some conclusions are given in the closing part.

II. THEORY

Particles and fields are equivalent since both are defined thorough their interaction with other particles and fields. This simple fact has been used in physics of inhomogeneous fluids to derive integral equations theories \[38\], i.e., in a nonuniform fluid the external field is taken as one more species of the fluid. Hence, one can use standard integral equations theories for uniform fluids based on the Ornstein-Zernike equation.

In the Ornstein-Zernike equation for inhomogeneous fluids, the total correlation function between an external field and a particle of the fluid, \(h_{\alpha\beta}(\mathbf{r}_{21})\), is decomposed...
as the sum of direct and indirect correlations, i.e.,
\[ h_{\alpha i}(\mathbf{r}_{21}) = c_{\alpha i}(\mathbf{r}_{21}) + \sum_{k=1}^{n} \int \rho_{m} h_{\alpha m}(\mathbf{r}_{23}) c_{m i}(\mathbf{r}_{31}) d\mathbf{r}_{3} \]  
(1)

where \( c_{\alpha i}(\mathbf{r}_{21}) \) represents the direct correlation function between the external field and a particle of species \( i \) located at \( \mathbf{r}_{21} \) and \( c_{m i}(\mathbf{r}_{31}) \) is the direct correlation function between any pair of particles, of species \( m \) and \( i \), in the fluid. In this notation the subindex \( \alpha \) refers to the external field. The second term in Eq. (1) represents the indirect correlation between the external field with a particle of species \( i \), carried out through all the particles of species \( m \) in the fluid. The total correlation functions are related to the particles distribution functions, \( g_{\alpha i}(\mathbf{r}_{21}) \), by \( h_{\alpha i}(\mathbf{r}_{21}) = g_{\alpha i}(\mathbf{r}_{21}) - 1 \).

The Ornstein-Zernike equation requires extra relationships, referred to as closures, between \( h_{\alpha i}(\mathbf{r}_{21}) \) and \( c_{\alpha i}(\mathbf{r}_{21}) \) to be solved. Here, we apply the hypernetted chain/mean spherical approximation (HNC/MSA), which implies that \( c_{\alpha i}(\mathbf{r}_{21}) \) is approximated by the hypernetted chain (HNC) closure, whereas \( c_{m i}(\mathbf{r}_{31}) \) is taken through the mean spherical approximation (MSA). This approach has been applied for modelling inhomogeneous and confined electrolytes in many geometries and, in general, it has shown good agreement with computer simulations \cite{4,11,12}.

### A. The surface and fluid models

We consider an electrolyte solution contiguous to a planar wall which has a uniform surface charge density \( \sigma_{0} \) and dielectric constant \( \epsilon_{w} \) (See Fig. 1). In the restricted primitive model (RPM) electrolyte, the ions are considered as hard spheres of diameter \( a \), with a centered point charge \( q_{i} = e z_{i} (e \) is the proton’s charge and \( z_{i} \) is the ionic valence), and at concentration \( \rho_{i} \). The ions are embedded in a structureless solvent, considered only through a uniform medium of dielectric constant \( \epsilon \) and, for simplicity, \( \epsilon_{w} = \epsilon \). Within this model, a high particles volume fraction (large \( \alpha \) and/or high \( \rho_{i} \)) could be a simplistic way of taking into account solvent effects, such as solvation or excluded volume. In this regard, some recent works have considered the solvent effect through more refined models \cite{33,10}.

In planar geometry, \( g_{\alpha i}(\mathbf{r}_{21}) \) depends only of the perpendicular distance to the surface, \( x \), therefore hereinafter we will simply write \( g_{i}(x) \equiv g_{\alpha i}(\mathbf{r}_{21}) \) and \( h_{\alpha m}(y) \equiv h_{\alpha m}(\mathbf{r}_{23}) \), where the subindex \( \alpha \) has been omitted. The charge on the wall is compensated by an excess of charge in the fluid given by the charge density profile, \( \rho_{el}(x) \), such that

\[ -\sigma_{0} = \int_{a/2}^{\infty} \rho_{el}(x) dx \]  
(2)

The charge density profile gives the structure of the electric double layer (EDL) and it is expressed in terms of the ions distribution functions, \( g_{i}(x) \), as

\[ \rho_{el}(x) = \sum_{i=1}^{2} z_{i} e \rho_{i} g_{i}(x) \]  
(3)

The surface-ion direct interaction potential is written as \( u_{\alpha i}(x) = u_{el}^{i}(x) + u_{el}^{\alpha i}(x) \), where the first term is the ion-surface hard-core interaction potential which considers that ions can not penetrate or deform the surface. The second term is the electrostatic contribution, given by

\[ u_{el}^{i}(x) = -\frac{2\pi}{\epsilon} q_{i} \sigma_{0} (x - x_{\infty}) \]  
(4)

being \( x_{\infty} \) a reference point.

The \( i \) species concentration profile, \( g_{i}(x) \), is related to the ion-wall potential of mean force, \( w_{i}(x) \), by

\[ g_{i}(x) = \exp \{ -\beta w_{i}(x) \} \]  
(5)

from which the ion-wall effective mean force, \( f_{xi}(x) \), is obtained by

\[ f_{xi}(x) = -\frac{\partial w_{i}(x)}{\partial x} = k_{B} T \frac{\partial \ln g_{i}(x)}{\partial x} \]  
(6)

From this relationship one can infer that a negative (positive) slope of \( g_{i}(x) \) requires an attractive (repulsive) behavior of \( f_{xi}(x) \).

The computation of \( g_{i}(x) \) requires to solve Eq. (1). As we pointed out above, it is solved by approximating \( c_{i}(x) \equiv c_{\alpha i}(\mathbf{r}_{21}) \) by the hypernetted chain closure in Eq. (1), i.e.,

\[ c_{i}(x) = -\ln g_{i}(x) - \beta u_{i}(x) + h_{i}(x) \]  
(7)
Thus, by combining Eqs. (7) and (11) we get

\[ g_i(x) = \exp \left\{ -\beta u_{\alpha i}(x) + \sum_{m=1}^{2} \rho_m \int h_m(y) c_{mi}^{\text{MSA}}(s) \, ds \right\} \]  
(8)

In addition, in Eq. (8), we used the bulk MSA direct correlation functions between two ions of species \( i \) and \( m \), i.e., \( c_{mi}^{\text{MSA}}(s) \), with \( s = |r_{31}| \) their relative separation distance. As usual, \( \beta = 1/(k_B T) \), where \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. The explicit form of \( c_{mi}^{\text{MSA}}(s) \) for the RPM electrolyte can be written as

\[ c_{mi}^{\text{MSA}}(s) = c_{\text{hs}}(s) + q_m q_i c_{\text{sr}}(s) - \frac{\beta q_m q_i}{\epsilon s} \]  
(9)

where \( c_{\text{hs}}(s) \) and \( c_{\text{sr}}(s) \) are short range functions, being equal to zero for \( s > a \). By integrating Eq. (8) in cylindrical coordinates, after some algebra it is written as

\[
g_i(x) = \exp \left\{ \frac{4\pi \beta}{\epsilon} z_i e \sigma_0 x + 2\pi \int_{a/2}^{\infty} h_s(y) K(x, y) dy \right. \\
+ J(x) + 2\pi z_i \int_{a/2}^{\infty} h_d(y) L(x, y) dy \\
+ \left. \left( \frac{2\pi \beta e^2 z_i}{\epsilon} \right) \int_{a/2}^{\infty} h_d(y) [x + y + |x - y|] dy \right\} \]  
(10)

with \( i = 1, 2 \) and defining \( h_s(y) = \sum_{m=1}^{2} \rho_m h_m(y) \),

\[ h_d(y) = \sum_{m=1}^{2} \frac{r_m}{r_{1m}} h_m(y) \]

and

\[ K(x, y) = \int_{|x-y|}^{\infty} c_s(s) ds \\
L(x, y) = \int_{|x-y|}^{\infty} c_{\text{sr}}(s) ds \\
J(x) = -2\pi \rho_T \int_{x-a}^{a/2} K(x, y) dy \]

where \( \rho_T = \sum_{i=1}^{2} \rho_i \) and it has been used that \( h_j(x) = -1 \) for \( x \leq a/2 \). The HNC/MSA integral equations, Eq. (10), can be conveniently written as

\[ g_i(x) = \exp \left\{ -\beta w_i(x) \right\} = \exp \left\{ -\beta q_i \psi(x) + w_{\text{sr}}(x) \right\} \]  
(11)

where \( \psi(x) \) is the mean electrostatic potential, expressed as,

\[ \psi(x) = -\frac{4\pi}{\epsilon} \sigma_0 x - 2\pi \int_{a/2}^{\infty} \rho_{\text{ei}}(y) [x + y + |x - y|] dx \]  
(12)

and \( w_{\text{sr}}(x) \) is a short range potential, given by,

\[ w_{\text{sr}}(x) = -2\pi \int_{a/2}^{\infty} h_s(y) K(x, y) dy - J(x) - 2\pi z_i \int_{a/2}^{\infty} h_d(y) dy \]  
(13)

In Eq. (13) size correlations are included through the first two terms, meanwhile, the last term includes electrostatic short range correlations. Thus, in the case of \( g_i = 0, \psi(x) = 0 \) and only the size correlations terms are included in Eq. (11), hence, the model reduces to the inhomogeneous hard-sphere fluid. On the other hand, in the point point limit \( (a = 0) \), \( w_{\text{sr}}(x) = 0 \) and Eq. (11) becomes

\[
g_i(x) = \exp \left\{ -\beta q_i \psi(x) \right\} = \exp \left\{ \frac{4\pi}{\epsilon} \sigma_0 \beta q_i x \\
+ \frac{2\pi \beta q_i}{\epsilon} \int_{a/2}^{\infty} \rho_{\text{ei}}(y) [x + y + |x - y|] dy \right\} \]  
(14)

which is the integral version of the Poisson-Boltzmann (PB) equation. In Eq. (14) a closest approach distance of the ions to the wall, \( a/2 \), is considered. PB equation for size-symmetric electrolytes does not predict CR since both, size and electrostatic short range correlations are neglected. However, it should be mentioned that models based on the PB equation may predict charge reversal when size correlations are considered artificially, i.e., by assigning to cations and anions unequal closest approach distances to the wall [13].

Eqs. (11) and (14) depend on several parameters, i.e., on \( \rho_i, a, T, \epsilon, z_i, \sigma_0 \). To simplify the analysis below we introduce the three fundamental parameters that describe the planar EDL.

### B. The fundamental parameters

The thermodynamical properties of the symmetric RPM electrolyte can be described exclusively in terms of the following parameters [28]

\[ \xi = \frac{q_i^2 \beta}{a \epsilon} \]  
(15)
\[ \eta = \frac{\pi}{6} \rho_T a^3 \]  
(16)

\( \xi \) accounts for strength of the ion-ion electrostatic interaction and is referred to as the ion-ion Coulomb coupling. The second parameter, \( \eta \), is the particles volume fraction. The ion-wall direct electrostatic interaction at the wall’s surface is given by

\[ U_i = q_i u_{\alpha i} \left( \frac{a}{2} \right) = \frac{2\pi q_i \sigma_0}{\epsilon} \left( x_\infty - \frac{a}{2} \right) \]  
(17)

thus, we define a third parameter

\[ \gamma_i = \frac{2\pi \beta}{\epsilon} q_i \sigma_0 a \]  
(18)

which quantifies the ion-wall electrostatic interaction. We also define \( \gamma \equiv |\gamma_i| \). It is an easy task to show that
total potential energy and the partition function function of the system (charged wall + electrolyte) can be written in terms of these dimensionless variables.

In terms of the $\gamma_i$ parameter, Eq. (11) can be written as

$$-\beta u_{ai}(X) = \frac{1}{2} \gamma_i (X - X_\infty)$$

with $X \equiv 2x/a$ the dimensionless distance. Hence, Eq. (10) is written as

$$g_i(X) = \exp \left\{ \gamma_i X + \int_1^\infty \hat{h}_{as}(Y) \hat{K}(X, Y) dY \right\}$$

+ $\hat{J}(X) + \hat{J}_\infty \int_1^\infty \hat{h}_{ad}(Y) \hat{L}(X, Y) dY$

+ $3 \hat{J}_\infty \int_1^\infty \hat{h}_{ad}(Y) [X + Y + |X - Y|] dY$ \hspace{1cm} (20)

where $\hat{J}_\infty \equiv q_j / q$ and we have defined

$$\hat{h}_{as}(X) = \sum_{m=1}^n \eta_m h_{am}(X)$$

$$\hat{h}_{ad}(X) = \sum_{m=1}^n \hat{z}_m \eta_m h_{am}(X)$$

The expressions for $\hat{K}(X, Y)$, $\hat{L}(X, Y)$ and $\hat{J}(X)$ are given below. For $X - 2 \leq Y \leq X + 2$,

$$\hat{K}(X, Y) = \frac{3}{4} c_1 [(X - Y)^2 - 4] + \frac{3}{2} \eta c_2 [X - Y|^3 - 8]$$

+ $\frac{3}{160} n c_1 [X - Y|^5 - 32]$

$$\hat{L}(X, Y) = \frac{3}{2} [2 - |X - Y|] - \frac{\Gamma_a}{2} \frac{\Gamma_a}{1 + \Gamma_a} [4 - (X - Y)^2]$$

+ $\frac{1}{4} \left( \frac{\Gamma_a}{1 + \Gamma_a} \right)^2 [8 - |X - Y|^3]$

otherwise $\hat{K}(X, Y) = \hat{L}(X, Y) = 0$. For $1 \leq X \leq 3$

$$\hat{J}(X) = \frac{1}{4} n c_1 [p^3 - 12p^2 + 16] + \frac{3}{8} \eta c_2 [p^4 - 32p + 48]$$

+ $\frac{1}{320} \eta^2 c_1 [p^6 - 192p - 320]$

otherwise $\hat{J}(X) = 0$, with $\hat{p} \equiv p - 1$. Eq. (20) is solved using a finite element technique. Details of the numerical method are given elsewhere. We wish to point out that the reduced concentration profiles, $g_i(X)$, depend only on the fundamental parameters $\xi$, $\eta$ and $\gamma$, for any combination of $\rho, a, T, \epsilon, \kappa, c_0$. That is, two systems are equivalent provided that $\eta, \xi$ and $\gamma$ are the same for both systems.

III. RESULTS AND DISCUSSION

The local electric field, $E(x)$, is useful to identify and quantify charge reversal. By Gauss' law it is given by

$$E(x) = \frac{4\pi}{\epsilon} [\sigma_0 + \sigma'(x)]$$

being $\sigma'(x)$ the surface charge density accumulated between two planes, parallel to the surface at $a/2$ and $x$, respectively, given by

$$\sigma'(x) = \int_{a/2}^x \rho_{el}(y) dy$$

The electroneutrality condition implies that $\lim_{x \to \pm \infty} \sigma'(x) = -\sigma_0$, such that the electric field produced by the plate is completely screened at infinity. In order to evaluate charge reversal (CR) we define the dimensionless function

$$\sigma(x) \equiv -\frac{\sigma_0 + \sigma'(x)}{\sigma_0}$$

such that CR occurs in an interval $[x_1, x_2]$ where $\sigma'(x)$ overcompensates $\sigma_0$, or equivalently, $\sigma(x) > 0$. Conveniently we also define $\sigma^*$ as the absolute maximum of $\sigma(x)$, i.e.,

$$\sigma^* \equiv \max\{\sigma(x) : x \in [a/2, \infty)\}$$

which, from Eq. (22), is written as

$$\sigma^* = -1 - \frac{1}{\sigma_0} \int_{a/2}^{x_{\max}} \rho_{el}(x) dx$$

being $x_{\max}$ the location of the absolute maximum of $\sigma(x)$. For the symmetric RPM electrolyte, which is the case considered here, $z_\pm = -z = z$ and $\rho_\pm = \rho_\pm = \rho_\pm$. Furthermore, it can be readily shown that the extreme values of $\sigma(x)$ are located at a set of points, $x_i$, where $\rho_{el}(x_i) = \sum_{i=1}^2 z_i \epsilon \rho_0 g_i(x_i) = 0$, implying $g_+(x_i) = g_-(x_i)$. It will be shown that the absolute maximum of $\sigma(x)$, $\sigma^*$, is the closest one to the wall. Thus, the plane at $x = x_{\max}$ defines the boundary of the adsorbed counterions layer and $\sigma^*$ quantifies the rate of charge overcompensation.

We constructed a charge reversal diagram in the $\eta$-$\xi$-$\gamma$ space in the following way: For a given constant value of $\gamma$ and starting from values of $\xi$ and $\eta$ close to zero, both parameters were progressively raised until the condition $\sigma^* > 0$ was reached (for numerical purposes we set $\sigma^* > 10^{-5}$). Hence, by repeating this procedure for different values of $\gamma$ the full space was analyzed. The onset of points of CR ($\eta^*, \xi^*$) define a curve referred to as the charge reversal curve. Thus, the main result of this work is presented in Fig. 2 the charge reversal diagram for the planar EDL. For clarity only three $\gamma$-dependent CR curves are plotted. For each value of $\gamma$, below the curve charge reversal does not occur whereas it does above it. It should be mentioned that $\sigma^*$ continues increasing for
higher values of either parameter, $\xi$ or $\eta$. Interestingly, for $0 < \gamma \lesssim 1$ all curves converge to the solid line. The dashed and dotted lines are for $\gamma = 5$ and $\gamma = 8$, respectively. Curiously, the three CR curves converge for $\xi \lesssim 1.7$. In general, as $\gamma$ increases the CR curves are shifted to the left. It should be mentioned that our diagram covers a broad range of the $\eta$-$\xi$-$\gamma$ space, including many cases of practical interest.

A least squares fitting in a log-log scale was carried out for the data composing the solid line of Fig. 2. Surprisingly, we found that they satisfy the simple relationship

$$10 \eta \xi = 0.0662,$$

or equivalently $24 \xi \eta = \kappa^2 a^2 \approx 1.6$, with $\kappa^2 = \frac{4 \pi \eta}{\varepsilon} \sum_{i=1}^{2} q_i^2 \rho_i$, the inverse Debye length. This curve splits the $\eta$-$\xi$ plane in two regimes: Regime I ($\xi \eta > 0.0662$) and regime II ($\xi \eta < 0.0662$). In regime I, CR occurs for any value of $\gamma$ different from zero, that is, CR is a property of the fluid due to the fact that the bulk ion-ion pair correlation function is oscillatory. This implies that any perturbation in the fluid (independently of the external field strength) is propagated in an oscillatory manner, producing alternated layers of counterions and cations next to the wall, hence, CR and CI. Although not shown, we found that this is valid for different geometries of the external field. In regime II, the ion-ion pair correlation function is monotonic, hence, the occurrence of CR depends on the external field. According to the behavior of the pair correlation function in bulk, regimes I and II are referred to as oscillatory and non-oscillatory, respectively.

The onset points of CR for some EDL systems, from molecular dynamics (b,f) and Monte Carlo (c) simulations, are plotted in the charge reversal diagram of Fig. 2. We also plotted the onset of oscillations of the ionic pair correlation function predicted by the dressed ion theory (DIT) (g,h) (See table I). It can be seen that our prediction ($\kappa \approx 1.260$, solid line) well agrees with the onset of oscillations of the pair correlation function predicted by DIT [30] ($\kappa \approx 1.293$), for a particular case of a monovalent RPM electrolyte (g). Our prediction is also in close agreement with the onset points of CR predicted by molecular dynamics (b,f) and Monte Carlo (c) simulations for several EDL systems of divalent electrolytes. For divalent electrolytes, our prediction is in better agreement with simulation data than DIT (h).

In Fig. 3, $\sigma$ is plotted, as a function of the dimensionless distance $X = 2\pi/q$, for $\xi = 6.72$, $\gamma = 2.4$ and $\eta = 0.01, 0.060.20, 0.30, 0.40$. Note that the number and amplitude of oscillations increase as $\eta$ increases. More importantly, however, is the fact that the absolute maximum of $\sigma(X)$, $\sigma^*$, increases by increasing $\eta$. A similar behavior is observed (not shown) if $\eta$ is constant and $\xi$ is increased. As we mentioned above, in Fig. 3, $\sigma^*$ is the closest maximum to the wall.

CR is not only governed by the ion-wall direct interaction, but above all, it is a many body effect in which long range and short range correlations participate. In Fig. 4, $\sigma^*$ is plotted as a function of

$$\zeta = \frac{\xi \eta}{\gamma} = \frac{z \eta}{2 \pi \sigma_0 a^2}$$

(26)

For the solid line the particles volume fraction $\gamma$ is raised and the Coulomb coupling parameters are kept constant at $\xi = 6.72$ and $\gamma = 2.4$. For the dashed line $\eta = 0.06, \gamma = 2.4$, and $\xi$ increases. Surprisingly, in both cases $\sigma^*$ increases monotonically with $\xi$ in a qualitatively similar way. In fact, for low values of $\zeta$ both curves are overlapped. In this sense we refer to electrostatic and size correlations as symmetric. This behavior, a priori, was not expected since $\eta$ and $\xi$ quantify contributions of different nature, i.e., size correlations ($\eta$) and electrostatic correlations ($\xi$), respectively. The symmetry is also exhibited in the charge reversal curves of Fig. 2 and par-
higher CR. pickeration and the higher effective excluded volume, hence, the higher value of ξη. For this particular case, the number of adsorbed counters per unit area, \( n^{cw} \), increases at a lower rate than \( n_{0} \), hence a decreasing behavior of \( \sigma^{*} \) is observed. For \( \xi = 2.04 \), a less pronounced, but also decreasing behavior of \( \sigma^{*} \) is seen. The former decreasing trend of \( \sigma^{*} \) vs \( \gamma \) is reversed for \( \gamma = 1.02 \). Curiously, the four shown curves cross at \( \gamma = 1.75 \), and below this point, \( \sigma^{*}(\eta = 1.02) < \sigma^{*}(\eta = 2.04) < \sigma^{*}(\eta = 4.08) < \sigma^{*}(\eta = 16.32) \). This in turn implies that \( \sigma^{*} \) is dominated by size correlations within this interval. Above this interval electrostatic correlations dominate. From this perspective, electrostatic and size correlations do not appear to be symmetric but, by contrary, are unsymmetrical. Both trends, increasing and decreasing, of the \( \sigma^{*} \) vs \( \gamma \) curves are supported by computer simulations in studies of CR in cylindrical [4] and spherical geometries [12].

IV. CONCLUSIONS

We studied the electrical double layer (EDL) of a planar wall next to a restricted primitive model electrolyte through a well established integral equations theory for inhomogeneous fluids, i.e., the hypernetted chain/mean spherical approximation (HNC/MSA). The HNC/MSA equations were derived in terms of the fundamental parameters of the system: the particles volume fraction, \( \eta = \frac{\beta q \sigma}{a^{3}} \), the ion-ion, \( \xi = \frac{2q^{2}}{\beta a^{2}} \), and ion-surface Coulomb coupling, \( \gamma = 2\pi \rho_{0} \beta q \sigma a / \epsilon \). To the best of our knowledge, for the first time a charge reversal diagram for the planar EDL is formally constructed. In this diagram two regimes of charge reversal are identified: In regime I (oscillatory) charge reversal occurs for any value of \( \gamma \) different from particular for \( \gamma \leq 1 (\xi \eta = 0.0662) \) when \( \eta (\xi) \) is low, a higher value of \( \xi (\eta) \) is needed to produce charge reversal.

From a fundamental point of view, the extra adsorption of particles to the wall, i.e., CR, implies a gain of entropy respect to the bulk [3, 4], thus, adsorption is favored. A simple way of understanding this, is through an analogy with the hard sphere model fluid next to a hard wall. In that case, size correlations induce adsorption of particles to the wall, which increases as the particle’s size or concentration increase, i.e., as \( \eta \) increases. In the HNC/MSA theory for a RPM electrolyte, electrostatic and size correlations are taken into account. Perhaps their symmetry (Figs. 2 and 3), can be explained by an effective excluded volume that mutual electrostatic repulsion between like charged ions confers them. Therefore, the higher value of \( \xi \), the higher the particles repulsion and the higher effective excluded volume, hence, the higher CR.
zero and independently of the external field geometry whereas, in regime II (non-oscillatory), a sufficiently high value of $\gamma$ is required. Using numerical analysis we found a simple formula which distinguishes these two regimes: regime I is defined by the condition $\xi\eta \geq 0.0662$, whereas the regime II is defined by $\xi\eta < 0.0662$. This simple formula for estimating when charge reversal is expected is relevant for colloid science, since oscillations of the charge profiles have been associated with an effective attractive interaction between like charged macroparticles [23, 24, 25]. The onset curve of charge reversal for the oscillatory regimes is in good agreement with the onset points of charge reversal obtained by molecular simulation for several EDL systems. Our study pointed out a symmetry in charge reversal between short range and electrostatic ionic correlations. The results of our study cover a broad range of practical interest.

Acknowledgments

F. J.-A. thanks Y. Duda and G. Odriozola for their critical reading and comments.

[1] Y. Levin, Rep. Prog. Phys. 65, 1577 (2002).
[2] W. M. Gelbart, R. F. Bruinsma, P. A. Pincus, and V. A. Parsegian, Physics Today 53, 38 (2000).
[3] P. Attard, J. Phys. Chem. 99, 14174 (1995).
[4] M. Deserno, F. Jiménez-Ángeles, C. Holm, and M. Lozada-Cassou, J. Phys. Chem. B 105, 10983 (2001).
[5] M. Tanaka and A. Y. Grosberg, J. Chem. Phys. 115, 567 (2001).
[6] T. Terao and T. Nakayama, Phys. Rev. E 63, 041401 (2001).
[7] T. Terao and T. Nakayama, Phys. Rev. E 65, 021405 (2002).
[8] F. Jiménez-Ángeles and M. Lozada-Cassou, J. Phys. Chem. B 108, 7286 (2004).
[9] F. Jiménez-Ángeles and M. Lozada-Cassou, J. Phys. Chem. B 108, 1719 (2004).
[10] R. Messina, C. Holm, and K. Kremer, Phys. Rev. Lett. 85, 872 (2000).
[11] R. Messina, C. Holm, and K. Kremer, Phys. Rev. E 64, 021405 (2001).
[12] R. Messina, E. González-Tovar, M. Lozada-Cassou, and C. Holm, Europhys. Lett. 60, 383 (2002).
[13] T. T. Nguyen, A. Y. Grosberg, and B. I. Shklovskii, Phys. Rev. Lett. 85, 1568 (2000).
[14] R. Kjellander, Ber. Bunsenges. Phys. Chem. 100, 894 (1996).
[15] J. Ennis, S. Marčelja, and R. Kjellander, Electrochimica Acta 41, 2115 (1996).
[16] G. Decher, Science 277, 1232 (1997).
[17] J. O. Rädler, I. Koltov, T. Salklitt, and C. R. Safinya, Science 275, 810 (1997).
[18] N. Cuvillier and F. Rondelez, Thin Solid Films 327-329, 10 (1998).
[19] M. Lozada-Cassou, E. González-Tovar, and W. Olivares, Phys. Rev. E 60, R17 (1999).
[20] M. Lozada-Cassou and E. González-Tovar, J. Coll. Int. Sci. 259, 285 (2001).
[21] M. Quesada-Pérez, E. González-Tovar, A. Martín-Molina, M. Lozada-Cassou, and R. Hidalgo-Álvarez, ChemPhysChem 4, 234 (2003).
[22] M. Tanaka, J. Phys. Condens. Matter 16, S2127 (2004).
[23] P.-Y. Hsiao and E. Luijten, Phys. Rev. Lett. 97, 148301 (2006).
[24] M. Lozada-Cassou and E. Díaz-Herrera, J. Chem. Phys. 93, 1386 (1990).
[25] P. Kékicheff, S. Marčelja, T. J. Senden, and V. E. Shubin, J. Chem. Phys. 99, 6098 (1993).
[26] F. Jiménez-Ángeles, G. Odriozola, and M. Lozada-Cassou, J. Phys. Chem. 124, 134902 (2006).
[27] K. Besteman, K. Van-Eijik, and S. G. Lemay, Nat. Phys. 3, 641 (2007).
[28] F. H. Stillinger and R. Lovett, J. Chem. Phys. 48, 3858 (1968).
[29] W. van Megen and I. Snook, J. Chem. Phys. 73, 4656 (1980).
[30] L. B. Bhuiyan, C. W. Outhwaite, and S. Levine, Mol. Phys. 42, 1271 (1981).
[31] M. Lozada-Cassou, R. Saaedra-Barrera, and D. Henderson, J. Chem. Phys. 77, 5150 (1982).
[32] G. M. Torrie and J. P. Valleau, J. Phys. Chem. 86, 3251 (1982).
[33] E. Gonzales-Tovar, M. Lozada-Cassou, and D. Henderson, J. Chem. Phys. 83, 361 (1985).
[34] P. Attard, J. Phys. Chem 99, 14174 (1995).
[35] H. Greberg and R. Kjellander, J. Chem. Phys. 108, 2940 (1998).
[36] J. Ennis, R. Kjellander, and D. J. Mitchell, J. Chem. Phys. 102, 975 (1995).
[37] R. Messina, C. Holm, and K. Kremer, Europhys. Lett. 51, 461 (2000).
[38] M. Lozada-Cassou, in Fundamentals of inhomogeneous fluids, edited by D. Henderson (Marcel Dekker, New York, 1993), Chap. 8.
[39] S. Gavryushov, J. Phys. Chem. B 111, 5264 (2007).
[40] S. Lamperski and A. Zydor, Electrochimica Acta 52, 2429 (2007).
[41] L. Degrève, M. Lozada-Cassou, E. Sánchez, and E. González-Tovar, J. Chem. Phys. 98, 8905 (1993).
[42] J. Yu and M. Lozada-Cassou, Phys. Rev. Lett. 79, 3656 (1997).
[43] J. Yu, G. E. Aguilar-Pineda, A. Antillón and S.-H. Dong, and M. Lozada-Cassou, J. Coll. Int. Sci. 294, 124 (2005).
[44] L. Mier y Terán, E. Díaz-Herrera, M. Lozada-Cassou, and R. Saaedra-Barrera, J. Comp. Phys. 84, 326 (1989).
[45] This is not a phase diagram since, from a thermodynamical point of view, charge reversal is not a phase.
[46] The linear fitting produced a curve of the form $\xi\eta^{0.00226} = 0.0662 \pm 0.0001$. 

This simple formula for estimating when charge reversal is expected is relevant for colloid science, since oscillations of the charge profiles have been associated with an effective attractive interaction between like charged macroparticles.