

Density functional theory study of electric potential saturation: Planar geometry

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We investigate the possibility of electrostatic potential saturation, which may lead to the phenomenon of effective charge saturation. The system under study is a uniformly charged infinite plane immersed in an arbitrary electrolyte made up of several microspecies. To describe the electric double layer, we use a generic local density functional theory in which the local microionic density profiles are arbitrary functions of the local electrostatic potential. A general necessary and sufficient condition is obtained for saturation, whereby the electrostatic potential created by the plane becomes independent of its bare charge, provided the latter is large enough. As a consequence, for most situations, the following simple and practical sufficient condition follows: if, as the electric potential $\psi \rightarrow \infty$, the local theory predicts that the highest valency counterions density diverges as ψ^ν with some $\nu > 1$ or faster, then the electrostatic potential will saturate. Otherwise, if the counterion density diverges as ψ or slower, or does not diverge as $\psi \rightarrow \infty$, the electric potential will not saturate. Using this condition, we investigate the possibility of the saturation phenomenon within the framework of recent theories proposed in the literature to describe electrical double layer beyond the Poisson-Boltzmann description.

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I. INTRODUCTION

The importance of effective charge in colloidal or polyelectrolyte suspensions has been recognized for some time [1–8]. The electric potential far from a colloid immersed in an electrolyte defining the inverse screening length κ takes the same form as the solution of the linearized Debye-Hückel equation—say $l_B Z_{\text{eff}} e^{-\kappa(r-R)}/[(1+\kappa R)r]$ for a charged sphere of radius R —but with a prefactor Z_{eff} which is different from the bare charge Z_{bare} of the colloid. In the previous expression, r is the distance from the center of the sphere of interest and $l_B = q^2/(\epsilon k_B T)$ is the Bjerrum length, defined from the elementary charge q and the permittivity ϵ of the solvent (the molecular structure of which is neglected). An interesting feature that occurs in the framework of (nonlinear) Poisson-Boltzmann theory [9] is that for highly charged colloids, the effective charge Z_{eff} saturates to a finite value Z_{sat} [7,10]. Interestingly, this saturation value is an upper bound for effective charges found within more refined approaches that incorporate the microionic correlations neglected in Poisson-Boltzmann theory [11]. We will come back to the validity of the latter approach in the concluding section.

Since Poisson-Boltzmann is a mean field theory, there have been several proposals to go beyond that approximation and try to include effects such as microions excluded volume [12–14] or electrostatic correlations between microions [15]. A natural question arises. Under which conditions a given theory will account for the saturation phenomenon? We will

not give here a definite answer to this question in its full generality. However we will consider the special case of local theories—theories which provide a local relationship between the density of microions and the electric potential—and give a necessary and sufficient condition under which the electrostatic potential of an infinite charged plane immersed in an electrolyte will saturate when the bare surface charge density of the plane diverges. This general condition is stated in Eqs. (4.1) and makes reference to functions defined in Eqs. (3.6), (3.3), and (2.3). From this condition follows the simpler and practical sufficient condition: if, as the electric potential $\psi \rightarrow \infty$, the local relationship between the highest valency counterions density n_γ and the electric potential becomes $n_\gamma \propto \psi^\nu$ for some $\nu > 1$ or n_γ diverges faster than any power law of ψ , then the electrostatic potential will saturate. Otherwise, if the counterion density diverges as ψ , or slower than ψ , or does not diverge, the electric potential cannot saturate.

As explained below, the phenomenon of potential saturation is slightly more general than that of effective charge saturation: effective charge saturation implies potential saturation, whereas potential saturation does not necessarily allow one to define an effective charge.

This paper is organized as follows. We will present in Sec. II the framework and the class of theories that will be considered. In Sec. III, we will formally integrate the generalization of Poisson-Boltzmann equation that these local theories yield. We will discuss in Sec. IV the necessary conditions to have the potential saturation effect. Finally, in Sec. V, we will apply our results to some recent theories [14,15] that have been proposed to go beyond the description of Poisson-Boltzmann theory.

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II. FRAMEWORK

Let us consider an infinite plane located at $x=0$ with a surface charge density σ . The half space $x>0$ is filled with an electrolyte made up of several species of microions with charges q_α and local densities $n_\alpha(x)$. We use Greek indices for the different species of microions. The system is in thermal equilibrium at an inverse temperature $\beta=(k_B T)^{-1}$. Without loss of generality we suppose $\sigma>0$.

The average electric potential $\psi(x)$ at a distance x from the charged plane is related to the densities of microions by Poisson equation

$$\psi''(x) = -\frac{4\pi}{\varepsilon} \rho(x). \quad (2.1)$$

The prime denotes differentiation with respect to x and $\rho(x) = \sum_\alpha q_\alpha n_\alpha(x) + \sigma \delta(x)$ is the total charge density. Furthermore the electric potential satisfies the boundary conditions

$$\psi'(0^+) = -4\pi\sigma/\varepsilon, \quad (2.2a)$$

$$\psi(\infty) = 0, \quad \psi'(\infty) = 0, \quad \psi''(\infty) = 0. \quad (2.2b)$$

Suppose now that an approximate local theory is provided. This theory gives local relations between the densities and the electric potential,

$$n_\alpha(x) = g_\alpha[q_\alpha \psi(x)], \quad (2.3)$$

which leads to a closed equation for the electric potential when we substitute Eq. (2.3) into Eq. (2.1):

$$\psi''(x) = -\frac{4\pi}{\varepsilon} \sum_\alpha q_\alpha g_\alpha[q_\alpha \psi(x)] \quad \text{for } x>0. \quad (2.4)$$

When $g_\alpha(u) = n_\alpha^b \exp(-\beta u)$, with n_α^b the bulk density of the species α , we recover Poisson-Boltzmann equation. Equation (2.4) may then be considered as a generalized Poisson-Boltzmann equation.

The local relation (2.3) between the density and the electric potential may be obtained in the framework of the density functional theory (DFT) by a local density approximation (LDA). In this framework, the free energy functional is given by

$$\begin{aligned} \mathcal{F}(\{n_\alpha\}) = & \int_0^\infty f(\{n_\alpha(x)\}) dx \\ & + \frac{1}{2} \int_0^\infty \int_0^\infty \rho(x) \mathcal{G}(x, x') \rho(x') dx dx', \end{aligned} \quad (2.5)$$

where \mathcal{G} is $(-4\pi/\varepsilon)$ times the one-dimensional Laplacian Green function with the appropriate (Neumann) boundary conditions. We have $\psi(x) = \int_0^\infty \mathcal{G}(x, x') \rho(x') dx'$.

The minimization of functional (2.5) subject to the conservation of the total number of particles (controlled by Lagrange multipliers μ_α , the chemical potentials of microspecies) gives

$$q_\alpha \psi = -\frac{\partial f(\{n_\gamma\})}{\partial n_\alpha} + \mu_\alpha. \quad (2.6)$$

We assume that upon inverting these relations, one obtains a set of relations of form (2.3) between each density and the electric potential. Note that Eq. (2.3) is really a set of equations giving, for each α , an explicit relation between $n_\alpha(x)$ and the electric potential $\psi(x)$. In particular each relation involves only one density $n_\alpha(x)$. It can, however, include the charges q_γ and chemical potentials μ_γ of the other particles [12–14] but not the other local densities $n_\gamma(x)$.

Poisson-Boltzmann theory is recovered when the local part of the free energy is given by the ideal gas contribution $f(\{n_\alpha\}) = f_{\text{id}}(\{n_\alpha\}) = \beta^{-1} \sum_\alpha n_\alpha [\ln(n_\alpha \Lambda) - 1]$, where Λ is an irrelevant length (the de Broglie wavelength).

Relations (2.3) should obey a certain number of physical constraints, for instance, the local charge density $\rho(x)$ should vanish when $x \rightarrow \infty$. We will impose the following constraint to the functions g_α appearing in Eq. (2.3):

$$\sum_\alpha q_\alpha g_\alpha[q_\alpha \psi(x)] \psi'(x) > 0. \quad (2.7)$$

This condition will be used several times in the subsequent analysis. In Appendix A we show that, in the framework of the DFT, this condition is a consequence of the stability of the system, namely, $\partial^2 f(\{n_\alpha\}) / \partial n_\alpha \partial n_\gamma$ is positive definite.

III. FORMAL INTEGRATION OF THE GENERALIZED POISSON-BOLTZMANN EQUATION

Multiplying Eq. (2.4) by $\psi'(x)$, we get

$$\frac{d}{dx} \{[\psi'(x)]^2\} = -\frac{8\pi}{\varepsilon} \sum_\alpha q_\alpha g_\alpha(q_\alpha \psi) \frac{d\psi}{dx} \quad (3.1)$$

which allows for a first integration

$$\psi'(x) = -\sqrt{-\frac{8\pi}{\varepsilon} \sum_\alpha G_\alpha(q_\alpha \psi(x))}, \quad (3.2)$$

where we defined

$$G_\alpha(v) = \int_0^v g_\alpha(u) du \quad (3.3)$$

and we have used the boundary condition (2.2b) at $x \rightarrow \infty$. The choice of the minus sign in the right-hand side of Eq. (3.2) is dictated by the fact that $\sigma > 0$.

Note that condition (2.7) ensures that the term under the square root sign in Eq. (3.2) is positive. Indeed, Eq. (2.7) implies that $d[\psi'(x)^2]/dx < 0$, therefore $\psi'(x)^2$ is a decreasing function and never vanishes for x finite. Then, $\psi'(x)$ never changes sign and since $\sigma > 0$, $\psi'(x) < 0$ and we conclude that $\psi'(x)$ is monotonic and increasing. The electric field $-\psi'(x)$ is monotonically decreasing, always positive, and nonvanishing for x finite. This remark is in fact a consequence of this particular geometry of the general proof

on the absence of overcharging whereby electric double layers are described by a local density functional theory of form (2.5) [16].

Rewriting Eq. (3.2) as

$$\frac{d\psi}{\sqrt{-\frac{8\pi}{\varepsilon} \sum_{\alpha} G_{\alpha}(q_{\alpha}\psi)}} = -dx \quad (3.4)$$

allows one to formally integrate it, to obtain

$$F(\psi) = -(x + x_0) \quad (3.5)$$

with x_0 being a constant of integration and the indefinite integral

$$F(\psi) = \int^{\psi} \frac{\sqrt{\varepsilon} d\phi}{\sqrt{-8\pi \sum_{\alpha} G_{\alpha}(q_{\alpha}\phi)}}. \quad (3.6)$$

The solution for the electric potential is given by inverting relation (3.5):

$$\psi(x) = F^{-1}(-(x + x_0)). \quad (3.7)$$

The function $F(\psi)$ introduced in Eq. (3.6) has a few useful properties. It is the integral of a positive quantity, so that it is a strictly increasing function¹ of ψ for $\psi \in [0, \infty[$ which can be inverted: F^{-1} exists and it is also an increasing function. As a consequence $\psi(x) = F^{-1}(-(x + x_0))$ is a decreasing function of x .

The constant of integration x_0 is related to the surface charge density σ of the plane and is determined by the boundary condition (2.2a). An interesting feature is that this constant of integration comes as an additive offset for the position x . A change in σ (therefore in the constant of integration x_0) results in a translation of the curve $\psi(x) - x$ along the x axis. This allows a graphical determination of x_0 : plotting the function $F^{-1}(-x)$, the origin $x=0$ of the x axis should be such that $dF^{-1}(-x)/dx = -4\pi\sigma/\varepsilon$ at this new origin, thus satisfying the boundary condition (2.2a). Again, the stability condition (2.7) ensures that there is a unique solution for x_0 since $\psi'(x)$ is monotonic.

IV. ELECTROSTATIC POTENTIAL SATURATION

We will say that there is a saturation of the electrostatic potential if it is possible to have $\sigma \rightarrow +\infty$ with a finite solu-

¹We suppose that the function $F(\psi)$ exists for all values of $\psi > 0$. This will be the case if all the functions $G_{\alpha}(q_{\alpha}\psi)$ are defined for any value of ψ .

tion for $\psi(x)$ for all $x \neq 0$.² We emphasize that the notion of potential saturation is more general than that of effective charge saturation: to define an effective charge, one needs to show that the ionic profiles behave far from the wall as they would within a *linear* theory such as Debye-Hückel theory. The effective charge is then defined from the far field created by the charged object, as that required within a linear theory to obtain the same potential at large distances. Our analysis does not require such a limitation. However, in the case where the local theory is formulated in the framework of the DFT we show in Appendix B that, far from the charged wall, the theory reproduces the far field of the linear Debye-Hückel theory, provided that the Hessian matrix ($\partial^2 f / \partial n_{\alpha} \partial n_{\gamma}$) is positive definite.

The function $F(\psi)$ is strictly increasing in the interval $[0, +\infty[$. Therefore there are only two possibilities for the behavior of $F(\psi)$ when $\psi \rightarrow +\infty$ which, as we show below, distinguish between the cases of saturation and nonsaturation.

$$\text{if } \lim_{\psi \rightarrow +\infty} F(\psi) < +\infty, \text{ there is saturation;} \quad (4.1a)$$

$$\text{if } \lim_{\psi \rightarrow +\infty} F(\psi) = +\infty, \text{ there is no saturation.} \quad (4.1b)$$

Let us consider first case (4.1a). Let $\lim_{\psi \rightarrow \infty} F(\psi) = -x_{\infty} < +\infty$. The functions $F(\psi)$ and $\psi(x)$ are sketched in Fig. 1. For any finite value of $\sigma > 0$ the determination of the constant of integration x_0 gives $x_0 > x_{\infty}$ and as σ increases, x_0 approaches x_{∞} . The case $\sigma = +\infty$ corresponds to the choice $x_0 = x_{\infty}$. In the graphical way of determining the constant of integration explained before, this means that the origin of the x axis is chosen above x_{∞} if $0 < \sigma < +\infty$ and it approaches x_{∞} as $\sigma \rightarrow +\infty$. We have clearly the potential saturation phenomenon since for $\sigma = +\infty$, where the origin of the x axis is precisely at x_{∞} , we have a finite solution for the potential $\psi(x)$ for any value of $x > 0$.

In the second case (4.1b), x_{∞} recedes to $-\infty$. Again, for $\sigma > 0$ finite, the boundary condition (2.2a) yields a value for $x_0 > x_{\infty} = -\infty$, and as σ increases, x_0 decreases. We actually have $\lim_{\sigma \rightarrow +\infty} x_0 = -\infty$, i.e., the constant of integration should decrease to minus infinity to satisfy the boundary condition. But since $\psi(x) = F^{-1}(-(x + x_0))$ and $F^{-1}(+\infty) = +\infty$ the electric potential $\psi(x)$ is infinite for all values of x . There is no saturation of the potential.

In practice, for a general theory formulated in the framework of a local DFT, it is not always easy to invert Eq. (2.6) in order to have an explicit expression (2.3) of the density as a function of the potential, and even more difficult to com-

²It is important to exclude $x=0$. Indeed, the limit $\sigma \rightarrow +\infty$ implies that $\psi'(0) = -\infty$ but since both ψ and ψ' are monotonic and $F(\psi)$ is supposed to exist for all values of $\psi > 0$, we also have $\psi(0) = +\infty$. The case of $\psi(0) > 0$ finite while $\psi'(0) = +\infty$ is ruled out by the conditions stated in footnote 1: if this was the case it would mean that integral (3.6) defining $F(\psi)$ would not be defined for values of $\psi > \psi(0)$ which implies that $\sum_{\alpha} G_{\alpha}(q_{\alpha}\psi_{\alpha})$ diverges to $-\infty$ for $\psi = \psi(0)$ and is not defined for $\psi > \psi(0)$.

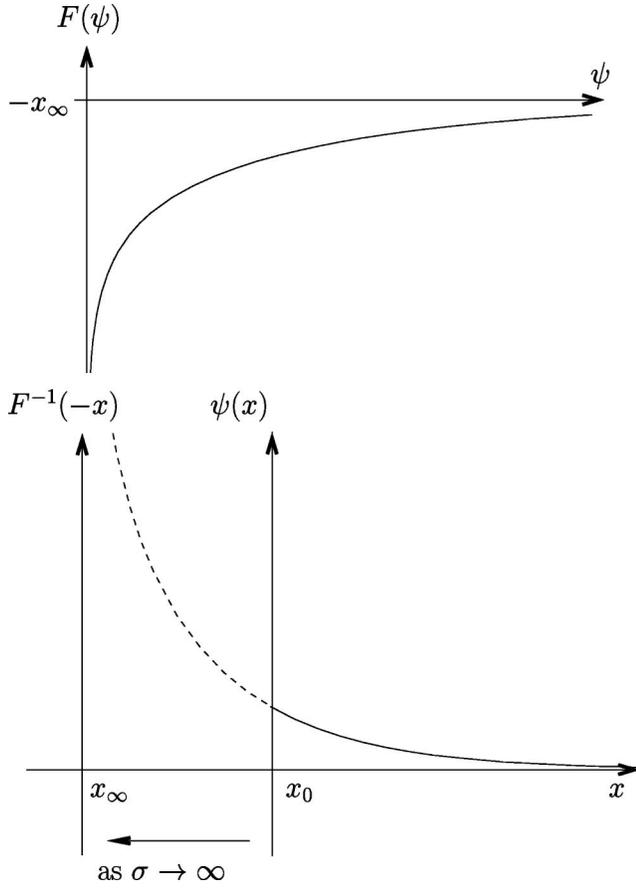


FIG. 1. An example of a theory in which the charge saturation phenomenon is possible. The upper figure represents the function $F(\psi)$ defined in Eq. (3.6) and in this example it has a finite limit when $\psi \rightarrow \infty$: $\lim_{\psi \rightarrow +\infty} F(\psi) = -x_\infty < +\infty$. The lower figure represents the inverse function $F^{-1}(-x)$. The plot of the electric potential $\psi(x)$ as a function of x is simply obtained choosing a new origin for the x axis, such that $dF^{-1}(-x)/dx = -4\pi\sigma/\epsilon$ at this new origin. For a given value of σ , only the part of the curve at the right of this origin (full line) has a physical meaning. When σ increases, this new origin gets translated to the left to finally reach the position of x_∞ when $\sigma = +\infty$.

pute the function $F(\psi)$ to study its limit as $\psi \rightarrow \infty$. However, there is no need to have explicitly the functions g_α of Eq. (2.3) to discuss the possibility of potential or charge saturation. Indeed, as shown below, we only need to know the behavior of the functions $g_\alpha(q_\alpha\psi)$ as $\psi \rightarrow +\infty$.

First we should treat the particular situation where it is possible to have from Eq. (2.3) or Eq. (2.6) an infinite potential $\psi \rightarrow +\infty$ while all the densities n_α are finite. If this is the case, then the functions $G_\alpha(q_\alpha\psi)$ behave as ψ —more precisely they are of order ψ which we denote $O(\psi)$ —when $\psi \rightarrow +\infty$. Therefore the integrand $[-\sum_\alpha G_\alpha(q_\alpha\psi)]^{-1/2}$ in Eq. (3.6) defining the function $F(\psi)$ behaves as $\psi^{-1/2}$ —more precisely $\psi^{-1/2} = O[-\sum_\alpha G_\alpha(q_\alpha\psi)]^{-1/2}$ —as $\psi \rightarrow +\infty$ and it is not integrable. We have $\lim_{\psi \rightarrow +\infty} F(\psi) \rightarrow \infty$. We then conclude that there is no saturation. To summarize, if a local theory predicts the possibility of having all densities of the microions finite when $\psi \rightarrow \infty$, this theory will consequently not account for the phenomenon of charge saturation.

Now, in the opposite case where the theory predicts that at least one density n_α —the density of counterions—diverges when $\psi \rightarrow \infty$, the existence of the saturation effect depends on how this density diverges as $\psi \rightarrow \infty$. If several densities diverge, actually what is important is the one that diverges the fastest as $\psi \rightarrow \infty$, say n_γ . Remembering that $n_\gamma(x) = g_\gamma(q_\gamma\psi)$, suppose that $g_\gamma(q_\gamma\psi)$ diverges as a power law ψ^ν . We prove below that if $\nu > 1$, then the effect of charge saturation will be accounted for by the theory, otherwise it will not. The argument is simple: suppose $g_\gamma(q_\gamma\psi)$ behaves as ψ^ν when $\psi \rightarrow \infty$, then $G_\gamma(q_\gamma\psi)$ behaves as $\psi^{\nu+1}$. The integrand in Eq. (3.6) behaves as $\psi^{-(\nu+1)/2}$ as $\psi \rightarrow \infty$ and is therefore integrable if and only if $(\nu+1)/2 > 1$, that is, $\nu > 1$. It is also clear from this argument that in the cases where the behavior of $g_\gamma(q_\gamma\psi)$ is not a power law of ψ but diverges faster than ψ^ν for some $\nu > 1$ there will be a saturation of the electric potential and in the cases where it diverges as ψ or slower, the electric potential will not saturate.

The remaining cases, where $g_\gamma(q_\gamma\psi)$ diverges faster than ψ but slower than ψ^ν for any $\nu > 1$, can always be resolved by returning to the study of the behavior of $[-G_\gamma(q_\gamma\psi)]^{-1/2}$ when $\psi \rightarrow \infty$ —the dominant part of the integrand of $F(\psi)$ in Eq. (3.6)—and determine if it is integrable or not.³

In the case where the electric potential saturates, the effective charge at saturation can be expressed in terms of the function $F(\psi)$ defined by Eq. (3.6). Let us consider the saturation regime and suppose that one can define an effective charge at saturation, i.e., the far field created by the plane has the same form as the one predicted by the linear Debye-Hückel theory (see Appendix B for details). This means that if $\psi \rightarrow 0$ we have $-(4\pi/\epsilon)\sum_\alpha q_\alpha g_\alpha(q_\alpha\psi) \sim \kappa^2\psi$ so that for $x \rightarrow \infty$,

$$\psi(x) \sim \psi^{\text{sat}} e^{-\kappa x} \quad (4.2)$$

with ψ^{sat} related to the effective charge at saturation by the relation $\psi^{\text{sat}} = 4\pi\sigma_{\text{eff}}^{\text{sat}}/(\kappa\epsilon)$. At saturation, in the graphical way of determining the constant of integration x_0 , the origin is at x_∞ . That is, $x_\infty = 0$ and

$$-x = F(\psi) \quad (4.3)$$

with the particular choice

$$F(\psi) = \int_{+\infty}^{\psi} \frac{d\phi}{\sqrt{-\frac{8\pi}{\epsilon} \sum_\alpha G_\alpha(q_\alpha\phi)}} \quad (4.4)$$

in the lower limit of integration. To be consistent with Eq. (4.2), we must have $F(\psi) \sim \kappa^{-1} \ln(\psi/\psi^{\text{sat}})$ for $\psi \rightarrow 0$. Therefore we can extract effective charge at saturation from

³For example, there could be cases such as $[-G_\gamma(q_\gamma\psi)]^{-1/2} \propto (\psi \ln \psi)^{-1}$ (not integrable) in which there will not be a saturation of the potential or cases such as $[-G_\gamma(q_\gamma\psi)]^{-1/2} \propto (\psi (\ln \psi)^2)^{-1}$ which is integrable and there will be a saturation.

$$\psi^{\text{sat}} = \frac{4\pi\sigma_{\text{eff}}^{\text{sat}}}{\kappa\epsilon} = \lim_{\psi \rightarrow 0} \{ \psi \exp[-\kappa F(\psi)] \}. \quad (4.5)$$

V. SOME EXAMPLES

In this section we apply our results to some local theories proposed in the literature. We first illustrate the results of the preceding section with some simple examples. We consider two cases (as benchmarks, since the analytic solution of the problem is known): Poisson-Boltzmann theory and its linearized counterpart, Debye-Hückel theory.

For Poisson-Boltzmann theory, $g_\alpha(q_\alpha\psi) = n_\alpha^b \exp(-\beta q_\alpha\psi)$, then the integrand in Eq. (3.6) behaves as $\exp(-\beta|q_0|\psi/2)$ when $\psi \rightarrow \infty$ and it is integrable (q_0 is the charge of the counterions with highest valency, which by the way have a density that diverges exponentially faster than the potential ψ). The function $F(\psi)$ has a finite limit when $\psi \rightarrow \infty$; we therefore recover there the well known fact that effective charge saturates when $\sigma \rightarrow \infty$.

For Debye-Hückel theory, $g_\alpha(q_\alpha\psi) = n_\alpha^b(1 - \beta q_\alpha\psi)$ behaves as ψ when $\psi \rightarrow \infty$ and the integrand in Eq. (3.6) behaves as ψ^{-1} , it is not integrable: there is no charge saturation.

Now let us turn our attention to some more interesting examples. Barbosa *et al.* [15] have proposed a local theory to account for counterions correlations in a one-component plasma (OCP) description of the electrolyte, that is, a system of charged counterions immersed in a uniform oppositely charged background. This theory, referred to as the Debye-Hückel-hole-cavity (DHHC) approach, is stable—it satisfies condition (2.7)—and the density n of the counterions is described in framework (2.5) of the DFT. The local free energy density is of the form $f(n) = f_{\text{id}}(n) + f_{\text{DHHC}}(n)$ where f_{id} is the ideal gas part of the free energy and

$$\frac{\beta f_{\text{DHHC}}(n)}{n} = \frac{(\kappa a)^2}{4} - \int_1^\omega d\bar{\omega} \left[\frac{\bar{\omega}^2 \Omega(\bar{\omega})^{2/3}}{2(\bar{\omega}^3 - 1)} + \frac{\bar{\omega}^3}{(1 + \Omega(\bar{\omega})^{1/3})(\bar{\omega}^2 + \bar{\omega} + 1)} \right]. \quad (5.1)$$

In this equation,

$$\Omega(\bar{\omega}) = (\bar{\omega} - 1)^3 + \frac{(\kappa a)^3}{3l_B\kappa} (\bar{\omega}^3 - 1), \quad \omega = (1 + 3l_B\kappa)^{1/3}, \quad (5.2)$$

and $\kappa = \sqrt{4\pi l_B n}$ is the inverse Debye length. The theory has a parameter a which may be interpreted as a sort of radius of the microions (nonstrictly speaking, because the counterion density can actually be higher than a^{-3}).

Expression (5.1) is quite complicated and there is no hope to be able to obtain an analytical solution for the function $F(\psi)$ or even invert the relationship between the potential and the density obtained from the stationary equation (2.6). However we only need to investigate the limit $\psi \rightarrow \infty$.

First it is straightforward to see that if the density n is finite, the potential is finite. Now, if $n \rightarrow \infty$ we have

$\beta f_{\text{DHHC}}(n) \sim n^{5/3} a^2 (\pi/6)^{2/3}$ and it is the leading term in $f(n)$. The minimization equation (2.6) then yields $\beta|q|\psi \sim n^{2/3} a^2 (5/3) (\pi/6)^{2/3}$ for $n \rightarrow \infty$, so that for $\psi \rightarrow \infty$, we have

$$n \sim \frac{6}{\pi} \left(\frac{3}{5} \right)^{3/2} a^{-3} (\beta|q|\psi)^{3/2}. \quad (5.3)$$

The important fact is that the density of counterions behaves as ψ^ν with $\nu = 3/2 > 1$. This theory therefore leads to a saturation of the electrostatic potential, and more precisely to a saturation of effective charge.⁴

On the other hand there are theories that do not account for the saturation effect. As an example, let us consider the approach proposed by Borukhov and co-workers [12–14]. This is a local theory which incorporates approximately steric effects due to volume exclusion between the microions of the electrolyte. The local part of the free energy is $f(\{n_\alpha\}) = f_{\text{id}}(\{n_\alpha\}) + f_{\text{exc}}(\{n_\alpha\})$ with an excess part involving the size a of microions:

$$\beta f_{\text{exc}}(\{n_\alpha\}) = \frac{1}{a^3} \left[1 - \sum_\alpha a^3 n_\alpha \right] \ln \left(1 - \sum_\alpha a^3 n_\alpha \right). \quad (5.4)$$

This theory is also stable, namely, $(\partial^2 f / \partial n_\alpha \partial n_\gamma)$ is positive definite [17] and, therefore, it satisfies condition (2.7). From Eq. (5.4), there is a higher bound for the value of the microions densities which is a^{-3} : when the counterions density approaches a^{-3} the electric potential ψ diverges. Therefore, according to the discussion of the preceding section, this theory does not allow the electrostatic potential to saturate.

Our approach also predicts, in the case of nonsaturation, whether the effective charge will grow faster or slower than the bare charge. Let us illustrate this point considering again the framework presented in Refs. [12–14]. To simplify the argument, we consider a two-component electrolyte with counterions/coions of charge $-q/q$ and bulk density n_b . Poisson's equation then takes the form

$$\beta q \psi''(x) = \kappa^2 \frac{\sinh(\beta q \psi)}{1 - \zeta + \zeta \cosh(\beta q \psi)}, \quad (5.5)$$

where $\zeta = 2n_b a^3$ and $\kappa = \sqrt{8\pi n_b l_B}$.

In this case it is possible to have finite counterion density when $\psi \rightarrow \infty$ and as discussed in the preceding section, the function $F(\psi)$ defined in Eq. (3.6) behaves as $\psi^{1/2}$ as ψ diverges. More precisely, we have here

$$F(\psi) = \left(\frac{a^3}{2\pi|q|} \right)^{1/2} \psi^{1/2} + O(1) \quad (5.6)$$

so that

⁴To allow for the definition of an effective charge, Poisson-Boltzmann generalized equation (2.4) should behave as Helmholtz equation ($\psi'' \propto \psi$) when $\psi \rightarrow 0$. This is discussed in Appendix B.

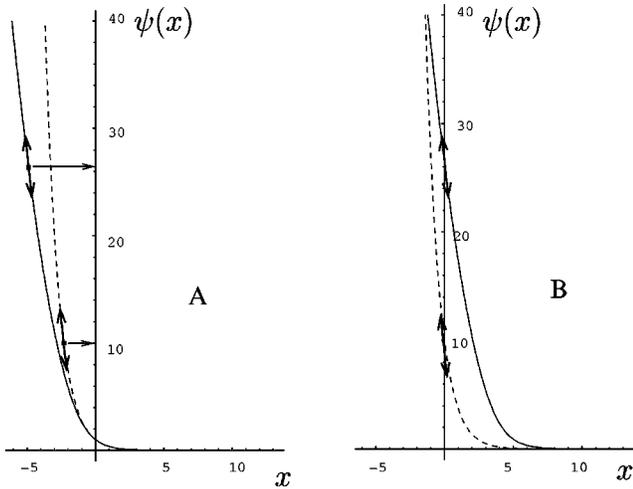


FIG. 2. Illustration of a theory (Refs. [12–14]) where the effective charge diverges faster than the bare charge. The dashed curve represents the potential $\psi_{\text{DH}}(x)$ predicted by Debye-Hückel theory and the full line represents the potential $\psi(x)$ put forward in Refs. [12–14]. The potential is measured in units of kT/q and the distance x in units of the Debye length κ^{-1} . We have chosen here $a^3 n_b = 1/4$, where n_b is the bulk density of ions. (A) A case where the bare charge σ is small [actually in the figure $4\pi\sigma\beta q/(\epsilon\kappa) = 1$]. Both curves have the same behavior as $x \rightarrow \infty$, namely, $\psi(x) = \exp(-x)$. (B) A case where σ is large [$4\pi\sigma\beta q/(\epsilon\kappa) = 10$]. To obtain (b) from (A), it is necessary to shift the curves by an amount indicated in (A) by the horizontal arrows. Since when $x \rightarrow -\infty$ the Debye-Hückel electric field increases exponentially, $-\psi'_{\text{DH}}(x) \sim \exp(-x)$, whereas the electric field of Refs. [12–14] increases only linearly, $-\psi'(x) \sim -x$, the curve for that last theory should be shifted to the right much more than the one for Debye-Hückel theory. This shows that the behavior at $x \rightarrow \infty$ is $\psi_{\text{DH}}(x) \sim 4\pi\sigma/(\epsilon\kappa)\exp(-x)$ and $\psi(x) \sim 4\pi\sigma_{\text{eff}}/(\epsilon\kappa)\exp(-x)$ with an effective charge larger than the bare charge $\sigma_{\text{eff}} > \sigma$.

$$F^{-1}(-x) \sim \frac{2\pi|q|}{a^3} x^2 \quad (5.7)$$

when $x \rightarrow -\infty$. On the other hand, one recovers Debye-Hückel theory for small potentials. This means that $F^{-1}(-x) \sim A \exp(-\kappa x)$ for $x \rightarrow \infty$ with A being an arbitrary constant since F is determined up to an additive constant. Suppose that initially the plane has a small bare charge density $\sigma^{(0)}$. For Debye-Hückel theory the electric potential reads $\psi_{\text{DH}}(x) = (4\pi\sigma^{(0)}/\epsilon\kappa)\exp(-\kappa x)$, so that $\epsilon\kappa A/(4\pi)$ may be considered as the effective charge describing the far field of the plane. As explained before, $\psi(x) = F^{-1}[-(x+x_0)]$ where the constant of integration x_0 can be determined graphically. Let us choose $A = 4\pi\sigma^{(0)}/(\epsilon\kappa)$, so that plots of $F^{-1}(-x)$ and $\psi_{\text{DH}}(x)$ superimpose when $x \rightarrow \infty$ (see Fig. 2). Now, consider a large bare charge density σ of the plane. To obtain from the curve of $F^{-1}(-x)$ the correct plot of $\psi(x)$ we should change the origin of the x axis such that the value of $dF^{-1}(-x)/dx = -4\pi\sigma/\epsilon$ at this new origin. Let us suppose σ large enough so that this new origin is in the region $x \rightarrow -\infty$ where $F^{-1}(-x)$ behaves as x^2 . As σ increases, we have to shift the origin further to the left or equivalently to

translate the curve of $F^{-1}(-x)$ to the right such that at the origin, both curves of $F^{-1}(-x)$ and ψ_{DH} have the same slope. But since $-\psi'_{\text{DH}}(x)$ behaves as $\exp(-\kappa x)$ which has a faster increase as $x \rightarrow -\infty$ than $-F^{-1}'(-x)$ which behaves as $-x$, it is clear that as σ increases we need to shift more to the right the curve of $F^{-1}(-x)$ than the one for $\psi_{\text{DH}}(x)$. On the other hand, for $x \rightarrow \infty$, we have $\psi(x) = B \exp(-\kappa x)$ with $B \propto \exp(-\kappa x_0)$. Since the translation of the curve of $F^{-1}(-x)$ becomes larger and larger than the one for $\psi_{\text{DH}}(x)$, this means that the factor B increases faster than the bare charge σ . The corresponding effective charge therefore increases faster than σ as σ is raised. We have also checked this feature from a direct numerical solution of Eq. (5.5). The above argument may be rationalized, as shown in Appendix C.

In the cases of nonsaturation, generalizing the argument presented before, if the faster divergent counterion density n_γ behaves slower than ψ when $\psi \rightarrow \infty$, then the theory will predict an effective charge that diverges faster than the bare charge. If, on the other hand, n_γ diverges faster than ψ —but slower than ψ^ν for any $\nu > 1$, so there is no saturation of the effective charge—then the effective charge will diverge slower than the bare charge.⁵

To sum up, a theory such as that of Refs. [12–14] cures a deficiency of Poisson-Boltzmann theory by setting an upper limit for the density of microions, at the expense of producing unphysical effective charges when the nonlinear character of the equation prevails (only for small electrostatic couplings would this theory give reasonable effective charges that would then coincide with the bare charge of the plane since the theory would reduce to Debye-Hückel theory). The same would happen for any DFT with the hard core part included through a local free energy density (one may wish, for instance, to use Carnahan-Starling-like expressions to account for excluded volume [18]): such approaches indeed lead to a divergence of the free energy density in the vicinity of close packing, so that $F(\psi) \propto \psi^{1/2}$ for large ψ . Since we have to expect that effective charges are bounded from above when the bare charge becomes large [11], the above analysis seems to show that when improving upon Poisson-Boltzmann theory, incorporation of steric effects through a local functional and/or neglect of microionic electrostatic correlations is insufficient.

VI. SUMMARY AND DISCUSSION

We have found a necessary and sufficient condition that a generic local density functional theory should fulfill to describe the effect of electrostatic potential saturation for a charged planar interface, namely, if in the local relation between the potential and the densities it is possible to have $\psi \rightarrow \infty$ and all densities finite, there will be no saturation. On the other hand, if as $\psi \rightarrow \infty$ the highest valency counterions density diverges as ψ^ν for some $\nu > 1$ or faster, the theory will predict a potential saturation. In the other case where the

⁵The first example of footnote 3 is a case where the divergence of the effective charge will be slower than the bare charge.

increase of the density is as ψ or slower, there will not be an electric potential saturation, hence no charge saturation. For the limiting cases where the density diverges faster than ψ but slower than ψ^ν for any $\nu > 1$ one should consider the general condition given in Eqs. (4.1): $[-\sum_\alpha G_\alpha(q_\alpha\psi)]^{-1/2}$, with G_α defined in Eq. (3.3), should be integrable as $\psi \rightarrow \infty$ to ensure that the electric potential saturates.

A natural continuation to this work would be to address the same question for a colloidal object of any shape. We expect that, for large colloids, the results found here will hold. However for small charged objects immersed in an electrolyte, the question remains open [23]. It would also be interesting to explore in more detail the behavior of effective charges in the framework of other theories, for instance, non-local theories.

At this point, it seems appropriate to come back to the validity of one of the simplest approaches encompassed by our formalism: Poisson-Boltzmann (PB) theory. In particular, it seems that the validity of the saturation regime within PB theory is sometimes confusing in the literature, which we might trace back to Onsager who wrote in a seminal paper [19] the following: ‘‘As soon as the higher order [non-linear] terms in the Poisson-Boltzmann equation become important, we can no longer expect the ionic atmosphere to be additive, and then the Poisson-Boltzmann equation itself becomes unreliable.’’

This statement (irrelevance of PB as soon as nonlinear behavior sets in) is justified for simple electrolytes, the system studied by Onsager in Ref. [19]. However, it turns incorrect when there is a large size and charge asymmetry between the constituents of a charged mixture, which is the case for colloidal suspensions [20]. This appears in the analytical work of Netz in the no salt limit [21]. Indeed, PB neglects correlations between microscopic species, which become prevalent at high electrostatic couplings, i.e., when $\Gamma = (q^3 \sigma l_B^2)^{1/2}$ becomes large [5,20–22]. On the other hand, PB enters the saturation regime when the coupling between the charged plane and the small ions becomes large, which may still be compatible with the neglect of microionic correlations, provided $\kappa l_B \ll 1$, as may be seen by replacing the saturation value $\sigma_{\text{sat}} \propto \kappa/l_B$ in the definition of Γ . A similar conclusion is reached enforcing that the correlational contribution to the pressure in the bulk of the electrolyte (the celebrated term in $-\kappa^3 k_B T$ appearing within Debye-Hückel theory of electrolytes [5,24]) should be negligible compared to the ideal gas contribution $n_b k_B T$: $\kappa^3 \ll n_b$ imposes $\kappa l_B \ll 1$.

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APPENDIX A

We prove here that condition (2.7) is a consequence of the stability of the theory formulated in the framework of the

local DFT (2.5). First, note that

$$\frac{d}{dx} \left[\sum_\alpha q_\alpha g_\alpha(q_\alpha\psi(x)) \psi'(x) \right] \quad (\text{A1a})$$

$$= \sum_\alpha q_\alpha n'_\alpha \psi' + \sum_\alpha q_\alpha n_\alpha \psi'' \quad (\text{A1b})$$

$$= - \sum_{\alpha,\gamma} \frac{\partial^2 f}{\partial n_\alpha \partial n_\gamma} n'_\alpha n'_\gamma - \frac{4\pi}{\epsilon} \rho^2, \quad (\text{A1c})$$

where we have used the minimization equation (2.6) and Poisson equation (2.1). If $(\partial^2 f / \partial n_\alpha \partial n_\gamma)$ is positive definite, this latter expression (A1a) is negative and therefore

$$\sum_\alpha q_\alpha g_\alpha(q_\alpha\psi(x)) \psi'(x) \quad (\text{A2})$$

is a decreasing function of x . Furthermore, the boundary conditions at $x \rightarrow \infty$ impose that Eq. (A2) vanishes at infinity, so that $\sum_\alpha q_\alpha g_\alpha[q_\alpha\psi(x)] \psi'(x) > 0$.

The condition that $\partial^2 f / \partial n_\alpha \partial n_\gamma$ is positive definite is a sufficient condition to ensure that Eq. (2.7) is satisfied. Let us remark that this same condition is sufficient for the nonexistence of like-charge attraction between colloids and the absence of overcharging [16]. It is also a sufficient condition for the compressibility of the system to be always positive within the cell model [25]. Furthermore, as it will be shown in Appendix B, it is a sufficient and necessary condition to recover Debye-Hückel linear theory where the electric potential is small.

APPENDIX B

In this appendix we prove that, far from the charged wall, any local theory reproduces the results of the linear Debye-Hückel theory provided that the Hessian matrix $\partial^2 f / \partial n_\alpha \partial n_\gamma$ is positive definite.

Far from the wall, the densities converge to their bulk values n_α^b and the potential vanishes. Then the minimization equation (2.6) for $\psi=0$ becomes $\mu_\alpha = (\partial f / \partial n_\alpha)_b$, where the subscript b means that the partial derivative of f is evaluated at the bulk values of the densities $n_\alpha = n_\alpha^b$. This provides the relationship between the chemical potentials and the bulk densities.

For small values of the potential, the difference $n_\alpha - n_\alpha^b$ is small, then we can expand

$$\frac{\partial f}{\partial n_\alpha} = \left(\frac{\partial f}{\partial n_\alpha} \right)_b + \sum_\gamma (n_\gamma - n_\gamma^b) \left(\frac{\partial^2 f}{\partial n_\alpha \partial n_\gamma} \right)_b + \dots \quad (\text{B1})$$

and substituting into the minimization equation (2.6) this gives

$$\sum_\gamma (n_\gamma - n_\gamma^b) \left(\frac{\partial^2 f}{\partial n_\alpha \partial n_\gamma} \right)_b = -q_\alpha \psi. \quad (\text{B2})$$

Provided that the Hessian matrix $(\partial^2 f / \partial n_\alpha \partial n_\gamma)_b$ is invertible we have

$$n_\alpha = n_\alpha^b - \sum_\gamma \left(\frac{\partial^2 f}{\partial n_\alpha \partial n_\gamma} \right)_b^{-1} q_\gamma \psi, \quad (\text{B3})$$

where $(\partial^2 f / \partial n_\alpha \partial n_\gamma)_b^{-1}$ denotes the (α, γ) matrix element of the inverse of the Hessian matrix $(\partial^2 f / \partial n_\alpha \partial n_\gamma)_b$.

Replacing into the generalized Poisson-Boltzmann equation (2.4) we obtain a Debye-Hückel-like equation

$$\psi''(x) = \kappa^2 \psi(x) \quad (\text{B4})$$

with an inverse Debye length κ^{-1} defined by

$$\kappa^2 = \frac{4\pi}{\varepsilon} \sum_{\alpha, \gamma} q_\alpha q_\gamma \left(\frac{\partial^2 f}{\partial n_\alpha \partial n_\gamma} \right)_b^{-1}. \quad (\text{B5})$$

To recover the results from Debye-Hückel theory, whatever the values of the charge q_α might be, it is necessary and sufficient that the Hessian matrix $(\partial^2 f / \partial n_\alpha \partial n_\gamma)_b$ is positive definite, which ensures the existence of its inverse and that $\kappa^2 > 0$.

APPENDIX C

In this appendix we prove that the theory presented in Refs. [12–14] predicts an effective charge that diverges exponentially faster than the bare charge when $\sigma \rightarrow \infty$.

The function defined by Eqs. (3.6) for the theory of Refs. [12–14] reads

$$F_{\text{BAO}}(\psi) = \frac{\beta q \zeta^{1/2}}{\sqrt{2} \kappa} \int_0^\psi \frac{d\phi}{\ln[1 - \zeta + \zeta \cosh(\beta q \phi)]} \quad (\text{C1})$$

while the one for Debye-Hückel theory is

$$F_{\text{DH}}(\psi) = \frac{1}{\kappa} \ln(\psi / \psi^{(0)}), \quad (\text{C2})$$

where in the last equation we have made the particular choice $\psi = \psi^{(0)}$ of the lower bound of integration in definition (3.6) of F_{DH} . Suppose that $\beta q \psi^{(0)}$ is chosen of the order one—say, $\beta q \psi^{(0)} = 1$. Now we choose the lower bound of integration in Eq. (C1) for F_{BAO} such that

$$F_{\text{BAO}}(\psi) = \kappa^{-1} \ln(\psi / \psi^{(0)}) + o(1), \quad \psi \rightarrow 0. \quad (\text{C3})$$

That is, $F_{\text{BAO}}(\psi)$ behaves as $F_{\text{DH}}(\psi)$ when $\psi \rightarrow 0$ up to terms that vanish when $\psi \rightarrow 0$. On the other hand we have behavior (5.6) for F_{BAO} when $\psi \rightarrow \infty$. Let us define $\psi_{\text{bare}} = 4\pi\sigma / (\kappa\varepsilon)$ and suppose that the bare charge σ of the plane is large enough such that $\beta q \psi_{\text{bare}} \gg 1$. For this value σ of the charge density of the plane, we have to find the constants of integration x_0^{BAO} and x_0^{DH} of Eq. (3.5) for the theory of Refs. [12–14] and for Debye-Hückel theory, respectively. We can proceed as follows: we first determine the value of $\psi^{\text{DH,BAO}}$ such that $F_{\text{DH,BAO}}(\psi^{\text{DH,BAO}}) = -x_0^{\text{DH,BAO}}$, then we deduce $x_0^{\text{DH,BAO}}$. For Debye-Hückel theory, applying the boundary condition (2.2a) we have

$$\left. \frac{d\psi}{dx} \right|_{x=0} = - \left(\frac{dF_{\text{DH}}}{d\psi} \right)^{-1} \Big|_{\psi=\psi^{\text{DH}}} = -\kappa \psi^{\text{DH}} = -\kappa \psi_{\text{bare}}. \quad (\text{C4})$$

Then for $\psi^{\text{DH}} = \psi_{\text{bare}}$ we have $F_{\text{DH}}(\psi^{\text{DH}}) = -x_0^{\text{DH}}$ and therefore $-\kappa x_0^{\text{DH}} = \ln(\psi_{\text{bare}} / \psi^{(0)})$. For the theory of Refs. [12–14] the boundary condition (2.2a) yields

$$\begin{aligned} \left. \frac{d\psi}{dx} \right|_{x=0} &= - \left(\frac{dF_{\text{BAO}}}{d\psi} \right)^{-1} \Big|_{\psi=\psi^{\text{BAO}}} \\ &\sim - \frac{2\kappa}{\sqrt{2}\zeta\beta q} \sqrt{\psi^{\text{BAO}}}, \quad \beta q \psi^{\text{BAO}} \gg 1 \\ &= -\kappa \psi_{\text{bare}}. \end{aligned} \quad (\text{C5})$$

Therefore we have $\psi^{\text{BAO}} \sim \zeta \beta q \psi_{\text{bare}}^2 / 2$ and $-\kappa x_0^{\text{BAO}} = \kappa F_{\text{BAO}}(\psi^{\text{BAO}}) \sim \zeta \beta q \psi_{\text{bare}}$. Clearly we have $x_0^{\text{BAO}} \gg x_0^{\text{DH}}$ as $\psi_{\text{bare}} \rightarrow \infty$. Furthermore these constants of integration manifest in the large- x behavior of $\psi(x)$ as $\psi(x) \sim \psi^{(0)} e^{-\kappa x_0} e^{-\kappa x}$ giving, for $x \rightarrow \infty$,

$$\psi_{\text{DH}}(x) = \psi_{\text{bare}} e^{-\kappa x} \quad (\text{C6})$$

for Debye-Hückel theory (as expected), while

$$\psi_{\text{BAO}}(x) \sim \psi^{(0)} e^{\zeta \beta q \psi_{\text{bare}} + o(\psi_{\text{bare}})} e^{-\kappa x}, \quad x \rightarrow \infty \quad (\text{C7})$$

for the theory of Refs. [12–14]. This theory predicts an effective charge that diverges exponentially fast when the bare charge $\sigma \rightarrow \infty$.

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