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Where the linearized Poisson-Boltzmann cell model fails: The planar case as a prototype study

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The linearized Poisson-Boltzmann (PB) approximation is investigated for the classical problem of two infinite, uniformly charged planes in electrochemical equilibrium with an infinite monovalent salt reservoir. At the nonlinear level, we obtain an explicit expression of the associated electrostatic contribution to the semi-grand-canonical potential. The linearized osmotic-pressure difference between the interplane region and the salt reservoir becomes negative in the low-temperature, large-separation, or high-surface charge limits, in disagreement with the exact (at mean-field level) nonlinear PB solution. We show that these artifacts—although thermodynamically consistent with quadratic expansions of the nonlinear functional—can be traced back to the nonfulfillment of the underlying assumptions of the linearization. Explicit comparison between the analytical expressions of the exact nonlinear solution and the corresponding linearized equations allows us to show that the linearized results are asymptotically exact in the weak-coupling and counterionic ideal-gas limits, but always fail otherwise, predicting negative osmotic-pressure differences. By taking appropriate limits of the full nonlinear PB solution, we provide asymptotic expressions for the semi-grand-canonical potential and the osmotic-pressure difference that involve only elementary functions, which cover the complementary region where the linearized theory breaks down.

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I. INTRODUCTION

The mean-field Poisson-Boltzmann (PB) approximation [1–5]—commonly used to describe aqueous suspensions of mesoscopic charged objects: membranes, clay platelets, polyelectrolytes, colloids, etc.—is known to yield incorrect results at the strong electrostatic coupling limit of low temperatures, high surfaces charges, or in the presence of multivalent counterions. We can fairly say that in the special geometry of two parallel, infinite charged walls separated by a simple electrolyte, the failures of the PB approach are well known from comparison to extensive Monte Carlo simulations [6] of the primitive model [7] (PM), where the molecular nature of the solvent is neglected and the short-ranged ion-ion interactions are taken as being of the hard-sphere type. These numerical studies show the existence of an attraction of purely electrostatic nature that is in apparent contradiction with the naive expectation based on the notion that two liked-charged macroscopic objects should repel each other. In fact, the exact solution of the nonlinear mean-field PB equation in planar geometry predicts only repulsive forces between like-charged objects [1–3], showing that it becomes inadequate to describe the attractions observed in the numerical simulations. Any theoretical explanation of these electrostatic-induced attractions in the planar geometry requires the introduction of effects beyond the mean-field level [8], as discussed later in the concluding remarks.

Related to the general question of effective attractive interactions between like-charged mesoscopic objects, there is still some controversy about their existence in deionized aqueous suspensions of like-charged spherical colloids, which would be mediated by monovalent counterions—see Ref. [9], and references therein. Even without the inclusion of effects beyond the mean-field level, several approaches based on approximations that involve some kind of linearization claim to theoretically explain this puzzling physical phenomenon [10]. These linearized results have been criticized based on the indications that the observed instabilities are artifacts due to the linearization, these being drastically suppressed when nonlinearities are reintroduced in the theory by the use of renormalized charges [11]. Furthermore, the linearization of the mean-field PB density functional for Wigner-Seitz cells yields artifacts [12,13] in the strong-coupling (low-temperature or high-surface charge) and infinite-dilution (of polyions) limits for the Donnan equilibrium problem [14–18], which describes a suspension of charged objects in electrochemical equilibrium with an infinite salt reservoir. In these limits the linearized osmotic-pressure difference between the suspension and the salt reservoir becomes negative, in disagreement with the full nonlinear PB result that always displays positive osmotic-pressure differences. We have shown, for the case of spherical polyions [9], that the instabilities observed in Refs. [12,13] are not related to thermodynamic inconsistencies, but are merely due to the application of the linearization scheme beyond its range of validity. In fact, the linearized equations agree asymptotically with the PB results in the weak-coupling (high-temperature or low-surface charge) limits. However, because the nonlinear PB equation is not analytically solvable in spherical geometry—even in the simplest salt-free case, when only neutralizing counterions are present—one must rely on numerical calculations to establish comparisons between the nonlinear and the linearized equations.

This motivated us to consider as a prototype case the classical problem of two uniformly charged infinite planes in electrochemical equilibrium with an infinite salt reservoir, where the exact analytical solution of the nonlinear problem is possible. We should emphasize that our main goal is neither to solve the nonlinear problem, nor to explain the attraction in the planar geometry using the linearized theory, but

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rather to test the range of validity of the linearization. The explicit analytical comparison between the exact (at the mean-field level) full nonlinear and the approximated linearized equations allows us to study in detail the breakdown of the linearization scheme. Since the linearized PB theory is extensively used—not only in the context of the controversial gas/liquid-type phase separation in colloidal suspensions considered in Ref. [9]—its detailed and careful analysis is worthwhile. This is especially instructive, because it is known *a priori* that the mechanisms of attraction in planar geometry cannot be described at the mean-field PB level, hence allowing us to expose the limitations and pitfalls of the linearization. Additionally, the study of this exactly solvable case clarifies the question of the proper definition of the linearized osmotic pressure that was previously considered in Ref. [13]. We will show that a linearized osmotic-pressure difference that might become negative—in contradiction with the nonlinear theory—is an unavoidable drawback of the linearized theory and just reflects the violation of the underlying physical assumptions of the linearization, namely, that the spatial variations of the electrostatic potential should be sufficiently small.

Moreover, to our knowledge, the explicit calculation of the semi-grand-canonical potential for two uniformly charged infinite planes at the nonlinear mean-field PB level has only been reported in connection to the polyelectrolyte-brush problem [19]. In that work, however, the thermodynamical potential also included electrostatic and elastic contributions arising from the polyelectrolyte brushes, and therefore, these need to be subtracted out. The knowledge of the PB nonlinear thermodynamic potential allows us to derive all thermodynamic properties of the two charged infinite planes problem at the mean-field level. We note that it can also be extended to curved surfaces by using the Derjaguin approximation [1,20,21]. It is then possible to determine the normal forces (per unit area) between these surfaces when their separation distance is much smaller than their curvature radius. In this work we will present the exact nonlinear semi-grand-canonical functional from which we derive approximate expressions. These involve only elementary functions and provide excellent approximations to the full nonlinear PB results within the whole range of parameters. We believe that these expressions are useful when treating problems under conditions where the effects of microionic correlations are unimportant, and additionally have planar geometry—e.g., charged membranes. In fact, the asymptotic expansions of the full nonlinear PB osmotic-pressure difference, presented in Sec. IV, provide higher-order terms and extend previous calculations by Pincus *et al.* [3,22].

The remainder of the paper is organized as follows. In Sec. II the model is introduced and the nonlinear equations are presented in a gauge-invariant form, suitable for a later comparison with the linearized ones. In Sec. III the linearization of the appropriate semi-grand-canonical functional is performed. In Sec. IV we present explicit analytic comparisons between the exact nonlinear and the linearized equations of state. In Sec. V we give some concluding remarks. Several technical points are relegated to Appendixes A to D.

II. NONLINEAR EQUATIONS

The system to be considered is comprised of two infinite planar surfaces a distance $2L$ apart, each with surface charge density $-\sigma q$, where $q>0$ is the elementary charge, in electrochemical equilibrium with an infinite monovalent salt reservoir of bulk salt density n_b. The microions (positive counterions and salt ions) are free to move in the region $-L<x<L$ between the two charged surfaces, where x measures the distance from the midplane located at $x=0$. In the PM it is implicitly assumed that the solvent dielectric constant ϵ remains the same outside the region containing the salt solution ($|x|>L$), so image-charge effects due to dielectric contrast are absent. At the mean-field level of approximation the ions are treated as inhomogeneous ideal gases described by their average local number densities $n_{\pm}(x)$. We do not distinguish between (positive) counterions and positive ions derived from the salt dissociation. The total charge number density (counterions, salt ions and the negative surface charge on the planes) of the system

$$\rho(x)=n_{+}(x)-n_{-}(x)-\sigma\delta(x+L)-\sigma\delta(x-L), \qquad (1)$$

where δ is the one-dimensional Dirac delta function, is related to the reduced electrostatic potential $\psi(x)\equiv\beta q\Psi(x)$, which satisfies the (exact) Poisson equation $d^2\psi(x)/dx^2=-4\pi l_B\rho(x)$, where $l_B\equiv\beta q^2/\epsilon$ is the Bjerrum length and $\beta^{-1}=k_BT$ is the thermal energy. The mean-field (nonlinear) semi-grand-canonical functional (for one charged plane) per unit area is given by [9]

$$\frac{\beta\Omega[n_{\pm}(x)]}{A}=\frac{1}{8\pi l_B}\int_0^L dx\left[\frac{d\psi(x)}{dx}\right]^2+\sum_{i=\pm}\int_0^L dx\, n_i(x)\times\left\{\ln\left[\frac{n_i(x)}{n_b}\right]-1\right\}, \qquad (2)$$

where the (mean-field) implicit microion chemical potentials $\beta\mu_{\pm}=\ln(n_b\zeta_{\pm}^3)$ assume ideal gases of uniform density n_b for both types of ions in the infinite salt reservoir and $\zeta_{\pm}$ are the thermal de Broglie wavelengths of cations (including the positive counterions) and anions.

The nonlinear equilibrium density profiles are obtained by minimizing the PB semi-grand-canonical functional (2) under the constraint of overall electroneutrality of the system

$$\lim_{\delta L\to 0_+}\int_0^{L+\delta L} dx\,\rho(x)=0, \qquad (3)$$

i.e., $[\delta/\delta n_{\pm}(x)][\Omega/A-\mu_{\mathrm{el}}\int dx\,\rho(x)]=0$, where the Lagrange multiplier μ_{el} ensures Eq. (3). This yields the Boltzmann-weighted ionic profiles

$$n_{\pm}(x)=n_b\exp[\pm\beta\mu_{\mathrm{el}}\mp\psi(x)]. \qquad (4)$$

The Lagrange multiplier μ_{el} is found by imposing the charge-neutrality condition (3). By inserting μ_{el} into the Boltzmann-weighted ionic profiles, Eqs. (4), it is now possible to write $n_{\pm}(x)$ in a gauge-invariant form [23]—i.e., in a form that does not depend on a particular choice of the zero of the electrostatic potential, but instead depend only on the difference $\langle\psi\rangle-\psi(x)$,

$$n_{\pm}(x)=\frac{\sqrt{n_c^2+(2n_b)^2\alpha_+\alpha_-}\pm n_c}{2\alpha_{\pm}}e^{\pm\langle\psi\rangle\mp\psi(x)}. \tag{5}$$

Here $n_c=\sigma/L$ is the average density of counterions in the interplane region $|x|<L$, $\alpha_{\pm}\equiv\langle e^{\pm\langle\psi\rangle\mp\psi(x)}\rangle$ and the brackets denote unweighted averages over the volume available to the microions, $\langle\mathcal{X}(x)\rangle\equiv(1/L)\int_0^L dx\,\mathcal{X}(x)$. In particular, in the salt-free ($n_b\to 0$) limit, these gauge-invariant forms lead—in a direct and transparent way—to the vanishing coion profile $n_-(x)\equiv 0$ and to the salt-free equilibrium counterion profile $n_+(x)=n_c e^{\langle\psi\rangle-\psi(x)}/\alpha_+$.

The most commonly used gauge [1,3] is the one in which the charge-neutrality Lagrange multiplier is zero, $\mu_{\mathrm{el}}\equiv 0$, which does not correspond to the gauge in which the electrostatic potential at the infinite salt reservoir vanishes [24]. In Appendix A we use the standard gauge $\mu_{\mathrm{el}}\equiv 0$ to treat the nonlinear problem, where we also give an explicit expression for the nonlinear semi-grand-canonical potential $\Omega\equiv\Omega[n_{\pm}(x)]_{\mathrm{equil}}$. We should keep in mind, however, that the fixed-gauge electrostatic potential $\varphi(x)\equiv\psi(x)-\beta\mu_{\mathrm{el}}$ will no longer be gauge invariant: its value at a particular point—let us say, at the midplane $\varphi_0\equiv\varphi(x=0)$ or at the charged surfaces $\varphi_L\equiv\varphi(x=L)$—will be determined by imposing the overall charge neutrality (3) in the whole system. They can no longer be chosen arbitrarily, in contrast to their gauge-invariant counterparts $\psi_0\equiv\psi(x=0)$ or $\psi_L\equiv\psi(x=L)$. On the other hand, in the gauge-invariant formulation, either ψ_0 or ψ_L may be chosen arbitrarily—but not both *simultaneously*—because the difference $\psi_L-\psi_0=\varphi_L-\varphi_0$ must eventually be preserved.

Finally we remark that the nonlinear osmotic-pressure difference between the interplane region and the salt reservoir $\Pi\equiv\beta\Delta P/(2n_b)=[n_+(0)+n_-(0)-2n_b]/(2n_b)$—given alternatively by Eq. (A16)—may also be written in a gauge-invariant form by using Eqs. (5),

$$\Pi=\left[\sqrt{\left(\frac{2}{\lambda l}\right)^2+\alpha_+\alpha_-}+\frac{2}{\lambda l}\right]\frac{e^{\langle\psi\rangle-\psi_0}}{2\alpha_+}+\left[\sqrt{\left(\frac{2}{\lambda l}\right)^2+\alpha_+\alpha_-}-\frac{2}{\lambda l}\right]\frac{e^{-\langle\psi\rangle+\psi_0}}{2\alpha_-}-1, \tag{6}$$

where the two dimensionless distances $\lambda\equiv\kappa_b\Lambda$ and $l\equiv\kappa_b L$ are defined in terms of two length scales: the Debye screening length associated with the bulk density n_b of the infinite salt reservoir

$$\kappa_b^{-1}\equiv\frac{1}{\sqrt{8\pi l_B n_b}} \tag{7}$$

and the Gouy-Chapman [25,26] length

$$\Lambda\equiv\frac{1}{2\pi l_B\sigma}, \tag{8}$$

which gives the characteristic (algebraic) decay length of the counterion distribution (for a salt-free system) around an infinite charged plane with bare surface charge σ. Although the gauge-invariant form (6) of the nonlinear osmotic-pressure difference seems to be cumbersome when compared to the simpler version given by Eq. (A16), it will be useful later, at the end of Sec. III, when establishing a connection between its quadratic expansion about the average potential $\langle\psi\rangle$ and its linearized counterpart (22).

III. LINEARIZED EQUATIONS

To obtain the linearized semi-grand-canonical functional $\Omega_{\mathrm{DH}}[n_{\pm}(x)]$ we truncate the expansion of the PB nonlinear semi-grand-canonical functional $\Omega[n_{\pm}(x)]$, Eq. (2), to second order in the differences $n_{\pm}(x)-\langle n_{\pm}(x)\rangle$, where $\langle n_{\pm}(x)\rangle\equiv(1/L)\int_0^L dx\,n_{\pm}(x)$ are the (*a priori* unknown) average densities. After minimization of the functional $\Omega_{\mathrm{DH}}[n_{\pm}(x)]$ with respect to the profiles $n_{\pm}(x)$ under the overall electroneutrality constraint (3), $[\delta/\delta n_{\pm}(x)][\Omega_{\mathrm{DH}}/A-\mu_{\mathrm{el}}\int dx\,\rho(x)]=0$, we obtain the self-consistent linearized averaged densities [9]

$$c_{\pm}^{(1)}\equiv\langle n_{\pm}^{(1)}(x)\rangle=\frac{\sqrt{n_c^2+(2n_b)^2}\pm n_c}{2} \tag{9}$$

and the linearized equilibrium density profiles

$$n_{\pm}^{(1)}(x)=c_{\pm}^{(1)}[1\pm\langle\psi(x)\rangle\mp\psi(x)], \tag{10}$$

where the superscript in $n_{\pm}^{(1)}(x)$ and $c_{\pm}^{(1)}$ emphasizes the fact that the self-consistent averaged densities (9) were obtained within a linearized approximation. Although similar quadratic expansions about the state-independent densities $c_{\pm}^{(1)}$ were already proposed for the planar case by Trizac and Hansen [27], they focused their study on finite-size effects and did not investigate the consequences of the linearization in detail. Deserno and von Grünberg [13] considered the general d-dimensional problem in a fixed-gauge formulation, interpreting these self-consistent linearized averaged densities in terms of an optimal linearization point $c_{\pm}^{(1)}=n_b e^{\mp\overline{\psi}_{\mathrm{opt}}}$.

The linearized expansion densities (9), which correspond to the zeroth order Donnan densities, represent the infinite-temperature ($l_B=0$) limit of the gauge-invariant forms of the equilibrium density profiles (5) and do not coincide with the exact nonlinear averages

$$c_{\pm}\equiv\langle n_{\pm}(x)\rangle=\frac{\sqrt{n_c^2+(2n_b)^2\alpha_+\alpha_-}\pm n_c}{2}=\frac{\sqrt{n_c^2+(2n_b)^2e^{\langle\delta_2(x)\rangle}+O[\langle\delta_3(x)\rangle]}\pm n_c}{2}, \tag{11}$$

because of the nonvanishing quadratic and higher-order ($\nu\geqslant 2$) contributions of the electrostatic-potential deviations

$$\delta_{\nu}(x)\equiv[\langle\psi\rangle-\psi(x)]^{\nu}. \tag{12}$$

In Appendix B we compare the linearized averages $c_{\pm}^{(1)}$, Eqs. (9), with their exact nonlinear counterparts $c_{\pm}$, Eqs. (11). We may anticipate that, as soon as the quadratic moment is small, $\langle\delta_2(x)\rangle\ll 1$, the full nonlinear equations will be very well described by the linearized ones. Moreover, we should remark that ensemble invariance will require the inclusion of quadratic contributions into the self-consistent averaged densities, leading to the definition of $c_{\pm}^{(2)}$—see Appendix D.

Inserting the linearized equilibrium density profiles (10) into the exact Poisson equation $d^2\psi(x)/dx^2 = -4\pi l_B \rho(x)$, yields the Debye-Hückel-like (DH-like) equation [28–31]

$$\frac{d^2\psi(x)}{dx^2} = \kappa^2[\psi(x) - \langle\psi(x)\rangle - \eta] + \frac{2}{\Lambda}[\delta(x+L) + \delta(x-L)], \tag{13}$$

where we introduced the parameter

$$\eta \equiv \frac{c_+^{(1)} - c_-^{(1)}}{c_+^{(1)} + c_-^{(1)}} = \frac{n_c}{\sqrt{n_c^2 + (2n_b)^2}}. \tag{14}$$

The (effective) Debye screening length in the interplane region κ^{-1} satisfies

$$\kappa^2 = 4\pi l_B [c_+^{(1)} + c_-^{(1)}] = \frac{\kappa_b^2}{\sqrt{1-\eta^2}} > \kappa_b^2, \tag{15}$$

showing that screening in the interplane region is enhanced compared to the salt reservoir. The gauge-invariant linearized electrostatic potential satisfying the DH-like Eq. (13) subject to the charge-neutrality constraint (3) reads

$$\psi(x) = \langle\psi(x)\rangle + \eta\left(1 - \kappa L\ \frac{\cosh\kappa x}{\sinh\kappa L}\right), \tag{16}$$

with the average electrostatic potential for an arbitrary electrostatic surface potential ψ_L given by

$$\langle\psi(x)\rangle = \psi_L + \eta\kappa L \mathcal{L}(\kappa L), \tag{17}$$

in terms of the Langevin function

$$\mathcal{L}(x) \equiv \coth x - \frac{1}{x}. \tag{18}$$

The linearized semi-grand-canonical potential $\Omega_{\rm DH} \equiv \Omega_{\rm DH}[n_{\pm}^{(1)}(x)]_{\rm equil}$ is obtained by inserting the equilibrium density profiles (10) and the DH-like solution (16) into the linearized semi-grand-canonical functional $\Omega_{\rm DH}[n_{\pm}^{(1)}(x)]$. After performing the integrations, we may cast the dimensionless excess linearized semi-grand-canonical potential per unit area in the form

$$\omega_{\rm DH}(\lambda, l) \equiv \frac{\kappa_b}{2n_b}\left[\frac{\beta\Omega_{\rm DH}(\Lambda, L)}{A} + 2n_b L\right] = \frac{2}{\lambda}\left[\operatorname{arctanh}\eta - \frac{1}{\eta} + \frac{1}{2}\eta k l \mathcal{L}(kl)\right] + l, \tag{19}$$

written in terms of the dimensionless length $k^{-1} \equiv \kappa_b \kappa^{-1}$ and recalling that λ and l were defined after Eq. (6). With these definitions we obtain the linearized self-energy $\omega_{\rm DH}(\lambda, l \to \infty) = 2/\lambda^2$ and

$$\eta = \eta(\lambda, l) = \frac{1}{\sqrt{1 + (\lambda l/2)^2}},$$

$$k^2 = k^2(\lambda, l) = \sqrt{1 + [2/(\lambda l)]^2} = \frac{1}{\sqrt{1 - \eta^2(\lambda, l)}}. \tag{20}$$

The dimensionless linearized osmotic-pressure difference $\Pi_{\rm DH} \equiv \beta\Delta P_{\rm DH}/(2n_b) = -d\omega_{\rm DH}(\lambda, l)/dl$,

$$\Pi_{\rm DH} = k^2\left\{1 + \eta^2\left(1 - \frac{3}{4}\eta^2\right) kl\ \mathcal{L}(kl) + \frac{1}{2}\eta^2\left(1 - \frac{1}{2}\eta^2\right) \times (kl)^2[\mathcal{L}^2(kl) - 1]\right\} - 1, \tag{21}$$

may be also obtained by performing a quadratic expansion of the gauge-invariant form of the nonlinear PB osmotic pressure (6)

$$\Pi_{\rm DH} = k^2\left[1 + \eta\delta_1(0) + \frac{1}{2}\delta_2(0) - \frac{1}{2}\eta^2\langle\delta_2(x)\rangle\right] - 1, \tag{22}$$

where the νth order electrostatic-potential differences (12) read

$$\delta_\nu(x) = \eta^\nu\left(\kappa L\ \frac{\cosh\kappa x}{\sinh\kappa L} - 1\right)^\nu. \tag{23}$$

In the next section we will investigate the properties of the linearized osmotic-pressure difference defined by Eqs. (21) or (22) and compare it with its exact nonlinear counterpart, Eqs. (6) or (A16).

IV. COMPARISON OF THE EXACT NONLINEAR AND THE LINEARIZED EQUATIONS OF STATE

As already pointed out in the literature [12,13], the linearized osmotic-pressure difference $\Pi_{\rm DH}$ defined by Eqs. (21) or (22) yields artifacts in the low-temperature, large-separation or high-surface charge limits. In contradiction to the exact nonlinear result (A16), which predicts that the osmotic-pressure difference is always positive, $\Pi > 0$, the linearized version $\Pi_{\rm DH}$ becomes negative in the above mentioned limits. In an attempt to define the osmotic pressure in a linearized framework, Deserno and von Grünberg introduced an additional (alternative) definition Π_1, cf. Eq. (43) of Ref. [13], that does not have the shortcoming of displaying any instabilities in the presence of symmetric electrolytes. On the other hand, we will show later that the osmotic-pressure definition that is partially unstable, cf. Eq. (44) of Ref. [13], coincides with the linearized version (21) obtained in the previous section $\Pi_2 \equiv \Pi_{\rm DH}$. The general formulas of Ref. [13] need to be taken, for the planar case $(d=1)$, in the formal limit of vanishing volume fraction $\phi \equiv a/L \to 0$—with $a > 0$ being some arbitrary length—which yields

$$\Pi_1 \equiv \frac{\beta P_1}{2n_b} - 1 = k^2\left[1+\eta\delta_1(0)+\frac{1}{2}\delta_2(0)\right]-1$$

$$= \frac{1}{2k^2}(k^2-1)^2+\frac{1}{2}\left(\frac{\eta k^2 l}{\sinh kl}\right)^2 \geqslant 0, \tag{24}$$

$$\Pi_2 \equiv \frac{\beta P_2}{2n_b}-1 = \Pi_1 - \frac{1}{2}k^2\eta^2\langle\delta_2(x)\rangle$$

$$= \Pi_1 - \frac{1}{4}k^2\eta^4\left(\frac{k^2l^2}{\sinh^2 kl}+kl\coth kl - 2\right). \tag{25}$$

The simpler formal forms of the two osmotic-pressure definitions are in accordance with Eqs. (23) and (26) of Ref. [13]. From them, one can see that the second osmotic-pressure definition coincides with the linearized osmotic-pressure difference (21) obtained in the last section, $\Pi_2 \equiv \Pi_{\rm DH}$, while the first one Π_1 differs from Eq. (22) by an omitted quadratic term. Analogously to the spherical case [9], the term that distinguishes the two distinct osmotic-pressure definitions originates from the volume dependence of the optimal linearization point $\bar{\psi}_{\rm opt} = -\operatorname{arctanh}\eta = -\operatorname{arccosh}k^2$, as pointed out by Deserno and von Grünberg [13].

From its asymptotic expansions to be given next and its formal expression (24), we see that Π_1, although fully thermodynamically stable for symmetric electrolytes—related to its positiveness, see Eq. (24)—is *inconsistent* with a quadratic expansion of the gauge-invariant nonlinear PB pressure (6), because of the omitted last quadratic term of Eq. (22). Furthermore, we will show next that the consistent—although partially unstable—linearized osmotic-pressure difference Π_2 presents indeed a better agreement with the nonlinear osmotic pressure Π in the weak-coupling and counterionic ideal-gas limits, when the underlying assumptions of the linearization are fulfilled. Therefore, although the alternative Π_1 displays the fortuitous advantage of preserving (for symmetric electrolytes) the positiveness of the exact nonlinear pressure Π, its derivation has no justification in our approach based on the minimization of the linearized semi-grand-canonical functional $\Omega_{\rm DH}[n_\pm(x)]$. Moreover, the partially unstable Π_2 corresponds indeed to the negative total derivative of the linearized semi-grand-canonical potential $\omega_{\rm DH}$ with respect to the planes separation l, which we thus believe to be the consistent and correct definition of the osmotic pressure.

Let us now perform an explicit comparison between asymptotic expressions of the nonlinear osmotic pressure, Π, and of the two corresponding linearized versions Π_1 and Π_2 for the distinct regimes listed below. We should remark that the asymptotic expressions of Π provide higher-order terms and extend previous calculations by Pincus *et al.* [3,22], see Ref. [32].

Weak-coupling or zeroth order Donnan ($l_B \to 0$) limit: $l \to 0$, $\lambda \to \infty$, but finite product λl

$$\Pi = k^2\left[1-\frac{\eta^2}{6}k^2l^2-\frac{\eta^2}{90}(\eta^2-3)k^4l^4+\frac{\eta^2}{945}(3\eta^2-5)k^6l^6 - \frac{\eta^2}{113400}(7\eta^6+18\eta^4+51\eta^2-84)k^8l^8+O(k^{10}l^{10})\right] - 1, \tag{26}$$

$$\Pi_1 = k^2\left[1-\frac{\eta^2}{6}k^2l^2+\frac{\eta^2}{30}k^4l^4-\frac{\eta^2}{189}k^6l^6+\frac{\eta^2}{1350}k^8l^8 + O(k^{10}l^{10})\right]-1, \tag{27}$$

$$\Pi_2 = k^2\left[1-\frac{\eta^2}{6}k^2l^2-\frac{\eta^2}{90}(\eta^2-3)k^4l^4+\frac{\eta^2}{945}(2\eta^2-5)k^6l^6 - \frac{\eta^2}{9450}(3\eta^2-7)k^8l^8+O(k^{10}l^{10})\right]-1. \tag{28}$$

Counterionic ideal-gas limit: $l \to 0$ and finite λ

$$\Pi = \frac{2}{\lambda l}\left\{1-\frac{l}{3\lambda}+\left(\frac{4}{45}+\frac{\lambda^4}{8}\right)\left(\frac{l}{\lambda}\right)^2-\frac{16}{945}\left(\frac{l}{\lambda}\right)^3 + O[(l/\lambda)^4]\right\}-1, \tag{29}$$

$$\Pi_1 = \frac{2}{\lambda l}\left\{1-\frac{l}{3\lambda}+\left(\frac{2}{15}+\frac{\lambda^4}{8}\right)\left(\frac{l}{\lambda}\right)^2-\frac{8}{189}\left(\frac{l}{\lambda}\right)^3 + O[(l/\lambda)^4]\right\}-1, \tag{30}$$

$$\Pi_2 = \frac{2}{\lambda l}\left\{1-\frac{l}{3\lambda}+\left(\frac{4}{45}+\frac{\lambda^4}{8}\right)\left(\frac{l}{\lambda}\right)^2-\frac{8}{315}\left(\frac{l}{\lambda}\right)^3 + O[(l/\lambda)^4]\right\}-1. \tag{31}$$

Gouy-Chapman or high-surface charge limit: $l \to 0$ and $\lambda/l \to 0$

$$\Pi = \frac{1}{2}\left(\frac{\pi}{l}\right)^2\left\{1-\frac{2\lambda}{l}+O[(\lambda/l)^3]\right\}-1+O(l^2), \tag{32}$$

$$\Pi_1 = \frac{2}{\lambda^2\sinh^2\sqrt{2l/\lambda}}+\frac{1}{\lambda l}-\frac{l^2\sqrt{2l/\lambda}\coth\sqrt{2l/\lambda}}{4\sinh^2\sqrt{2l/\lambda}}-1 + O(\sqrt{\lambda/l}), \tag{33}$$

$$\Pi_2 = \frac{1}{\lambda^2\sinh^2\sqrt{2l/\lambda}}-\frac{\coth\sqrt{2l/\lambda}}{\lambda^2\sqrt{2l/\lambda}}+\frac{2}{\lambda l}+O(\sqrt{l/\lambda}). \tag{34}$$

Large-separation limit: $l \to \infty$ and finite λ

$$\Pi=\frac{32e^{-2l}}{(\lambda+\sqrt{1+\lambda^2})^2}\left\{1-8\left[l-1+\frac{\lambda(1-\lambda^2)}{\sqrt{1+\lambda^2}}\right]\times\frac{e^{-2l}}{(\lambda+\sqrt{1+\lambda^2})^2}+O(l^2e^{-4l})\right\}, \tag{35}$$

$$\Pi_1=\frac{1}{\sinh^2 l}\left[\frac{2}{\lambda^2}-\frac{4\coth l}{\lambda^4 l}-\frac{2(1-3\coth^2 l)}{\lambda^6 l^2}+\frac{2(8+9\lambda^2-12\coth^2 l)\coth l}{3\lambda^8 l^3}\right]+\frac{2[1+O(e^{-2l})]}{\lambda^4 l^4}+O(l^{-5}), \tag{36}$$

$$\Pi_2=\frac{1}{\sinh^2 l}\left[\frac{2}{\lambda^2}-\frac{4\coth l}{\lambda^4 l}-\frac{2(1+2\lambda^2-3\coth^2 l)}{\lambda^6 l^2}\right]-\frac{4[1+O(e^{-2l})]}{\lambda^4 l^3}+O(l^{-4}). \tag{37}$$

Looking at Eqs. (34) and (37) one may see why the linearized osmotic-pressure difference Π_2 becomes negative at the Gouy-Chapman and large-separation limits. In the Gouy-Chapman limit the leading term is given by $\Pi_2 = O(\lambda^{-3/2}l^{-1/2})$, which is negative and overcomes the exponentially decaying $O(\lambda^{-2}e^{-2\sqrt{2l/\lambda}})$ contribution. The leading term of the large-separation limit is given by $\Pi_2 = O(\lambda^{-4}l^{-3})$, which is again negative and overcomes the exponentially decaying $O(\lambda^{-2}e^{-2l})$ contribution. In the full nonlinear solution, however, all power-law dependences on l cancel in a nontrivial way, and eventually only an exponentially (positive) decaying behavior $\Pi = O[e^{-2l}/(\lambda+\sqrt{1+\lambda^2})^2]$ is predicted. Note that both linearized versions Π_1 and Π_2 show asymptotic behaviors that disagree strongly from the nonlinear osmotic-pressure difference Π. This clearly indicates that both linearized osmotic-pressure definitions are meaningless in these limits and so is the positiveness of Π_1 in the presence of symmetric electrolytes.

We see that in the weak-coupling limit the self-consistent linearized osmotic pressure Π_2 and its nonlinear counterpart Π agree up to the $O(l^4)$ terms, confirming the validity of the linearization when its underlying assumptions are fulfilled. The same occurs for the counterionic ideal-gas limit up to the $O(l)$ terms. In both cases the fully stable Π_1 has a worse agreement, one order lower than the partially unstable Π_2. However, in the large-separation limit, the two linearized and the nonlinear expressions disagree even qualitatively: the linearized asymptotics are power laws on l, $\Pi_1 \propto l^{-4}$ and $\Pi_2 \propto -l^{-3}$, whereas the nonlinear is exponential (and positive) $\Pi \propto e^{-2l}$. On the other hand, although in the Gouy-Chapman limit all asymptotics are algebraic on l, in the linearized case the power laws are $\Pi_1 \propto l^{-1}$ and $\Pi_2 \propto -l^{-1/2}$, both in disagreement with the nonlinear asymptotics $\Pi \propto l^{-2}$. The failure of the linearization scheme should not be at all surprising, because it is supposed to be valid in the weak-coupling ($l_B \to 0$) and counterionic ideal-gas limits, but not in the opposite, large-separation ($l \to \infty$) or high-surface charge, Gouy-Chapman ($\lambda \to 0$) limits. Therefore, any results obtained in a linearized framework outside the weak-coupling and the counterionic ideal-gas limits should be taken with caution.

In order to show the accuracy of the self-consistent linearized osmotic-pressure difference Π_{DH}, Eq. (21), and the region where the linearization scheme breaks down, we plotted in Figs. 1 and 2 the locii of constant errors between the exact nonlinear PB osmotic-pressure difference and the corresponding linearized version, measured by the logarithmic deviations

$$\delta\Pi_{\mathrm{DH}} \equiv |\ln \Pi_{\mathrm{DH}}(\lambda,l)-\ln \Pi(\lambda,l)|. \tag{38}$$

We have chosen a logarithmic measure for the deviations because Π varies in a range of several orders of magnitude. For small deviations, this definition leads to the relative errors

$$\delta\Pi_{\mathrm{DH}} \approx \left|\frac{\Pi_{\mathrm{DH}}(\lambda,l)-\Pi(\lambda,l)}{\Pi(\lambda,l)}\right|. \tag{39}$$

Analogously, we may define the logarithmic deviation from PB of the linearized semi-grand-canonical potential

$$\delta\omega_{\mathrm{DH}} \equiv |\ln[\omega_{\mathrm{DH}}(\lambda,l)-\omega(\lambda,\infty)]-\ln[\omega(\lambda,l)-\omega(\lambda,\infty)]|, \tag{40}$$

which is always smaller than $\delta\Pi_{\mathrm{DH}}$ (not shown). Therefore the linearized semi-grand-canonical potential (19) and the linearized osmotic-pressure difference (21) describe well the corresponding nonlinear equations in the limit $\lambda/l \gg 1$ and $l \ll 1$. Because the nonlinear theory always predicts repulsion, the attractive osmotic-pressure region—shown in gray in Figs. 1 and 2—is clearly an artifact of the linearization. When plotted on the $\Lambda/L \times (\kappa_b L)^{-1}$ plane, the $\Pi_{\mathrm{DH}}=0$ line reaches at $\kappa_b L \to 0$ the asymptotic value $\xi_0 = \Lambda/L = 0.123863965\cdots$, which is given by the solution of the transcendental equation

$$2\xi_0+\sqrt{\frac{\xi_0}{2}}\mathcal{L}\left(\sqrt{\frac{2}{\xi_0}}\right)+\mathcal{L}^2\left(\sqrt{\frac{2}{\xi_0}}\right)=1. \tag{41}$$

To obtain the full nonlinear PB osmotic-pressure difference Π, one needs to numerically solve the transcendental equation (A8) involving elliptic functions or elliptic integrals. Although the asymptotic expansions of the nonlinear Π represented by Eqs. (26), (29), (32), and (35) allow an explicit analytical comparison in the distinct regimes with their linearized versions, they are not very useful for numerical evaluation. In Appendix C we derive extended expansions of the nonlinear PB semi-grand-canonical potential ω, Eq. (A14), and of the PB osmotic-pressure difference Π, Eq. (A16), that involve only elementary functions and are suitable for numerical implementation. These extend the numerical accuracy of the above mentioned asymptotic expansions of the full nonlinear Π and are complementary to the linear-

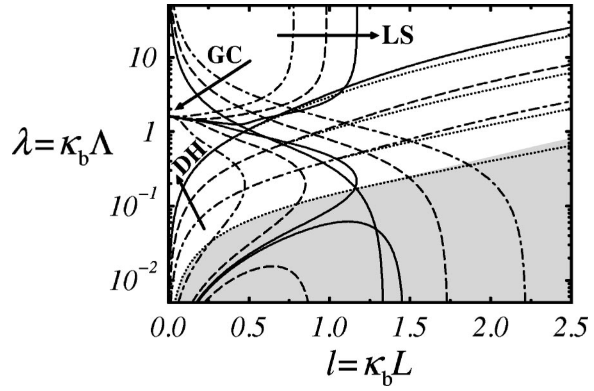

FIG. 1. Logarithmic deviations from the PB of the different asymptotic osmotic-pressure differences. DH represents the Debye-Hückel-like, linearized-functional expansion about the weak-coupling limit, GC corresponds to the expansion about the salt-free Gouy-Chapman limit, and LS denotes the large-separation limit expansion. The region complementary to LS is split into three branches. In the gray region the linearized osmotic-pressure difference Π_{DH} becomes negative. The arrows indicate the direction of decreasing logarithmic deviation $\delta\Pi$ from the PB results: 10^{-1} (dot-dashed lines), 10^{-2} (dashed lines), 10^{-3} (solid lines). For comparison, we also display (dotted lines) the linearized results by including quadratic contributions in the expansion densities, as defined by the linearized pressure $\hat{\Pi}_{\mathrm{DH}}$, Eq. (D3).

ized equations, ω_{DH}, Eq. (19), and Π_{DH}, Eq. (21), providing an excellent approximation in the regions where the linearization scheme breaks down. In Figs. 1 and 2 we also present their corresponding logarithmic deviations from the exact PB result, which, similarly to Eq. (38), are defined by

$$\delta\Pi_{\mathrm{GC}}\equiv|\ln\Pi_{\mathrm{GC}}(\lambda,l)-\ln\Pi(\lambda,l)|, \tag{42}$$

$$\delta\Pi_{\mathrm{LS}}\equiv|\ln\Pi_{\mathrm{LS}}(\lambda,l)-\ln\Pi(\lambda,l)|, \tag{43}$$

where Π_{GC} and Π_{LS}, given explicitly in Appendix C, are the osmotic-pressure differences in the extended Gouy-Chapman and extended large-separation limits, respectively.

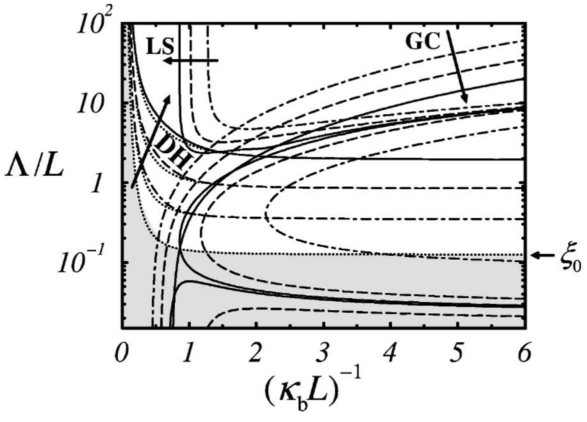

FIG. 2. Same as in Fig. 1, but plotted using different variables. At $\kappa_bL\rightarrow0$, the $\Pi_{\mathrm{DH}}=0$ line reaches the asymptotic value defined by Eq. (41), $\xi_0=\Lambda/L=0.123863965\cdots$. Compare with Fig. 1 from Ref. [22].

V. CONCLUDING REMARKS

The classical problem of two infinite uniformly charged planes in electrochemical equilibrium with an infinite salt-reservoir is exactly solved at the mean-field nonlinear level, as well as by a linearization scheme consistent with quadratic expansions of the nonlinear semi-grand-canonical functional. By using gauge-invariant forms of the electrostatic potential, we have shown that the linearized osmotic pressure corresponds to a quadratic expansion of the corresponding nonlinear version.

As already pointed out in the literature [13], it is shown that the self-consistent linearized osmotic pressure leads to artifacts in the large-separation and the Gouy-Chapman (high-surface charge) limits, predicting there negative osmotic-pressure differences. Although it is possible to define an alternative linearized osmotic pressure that is fully stable (in the presence of symmetric electrolytes) based on the partial derivative of the linearized semi-grand-canonical potential with respect to the separation distance [13], its stability is shown to be a fortuitous result. In fact explicit comparison of the exact nonlinear osmotic pressure and the two linearized versions shows that the linearized self-consistent osmotic pressure, though partially unstable, presents a better agreement with the PB results in the weak-coupling and counterion ideal-gas limits, where the linearization can be applied. However, not surprisingly, in the region where the linearization breaks down none of both proposed linearized osmotic pressures give quantitatively correct results.

To avoid confusion we should stress at this point the exactness of the PB nonlinear solution at the mean-field level and discuss its range of validity and limitations. It is known from numerical simulations of the PM [7] in the planar geometry that sufficiently close and highly charged planes in the presence of neutralizing counterions attract each other [33], even though for realistic charge densities and monovalent ions this is not observed at room temperature. In this case the attraction is prevented by steric repulsions at the small separations at which it would be observed neglecting the finite ionic size. Because the mean-field PB approximation always predicts repulsion, theoretical validation for this attraction (observed in fact at room temperature only for multivalent ions) has to be given beyond the PB level, e.g., by bulk counterion correlations [34,35], integral-equations theories [36,37], charge-correlation-induced attractions [38,39], charge-fluctuation-induced attractions [40–42], electrolytic depletion-induced attractions [43], discrete solvent-mediated attractions [44], field-theory methods [45], etc.—see also Refs. [46–55] for mechanisms of attraction between like-charged rods. On the other hand, in the strong-coupling limit the linearization of the WS-cell mean-field PB equation, as discussed in this work, does predict attraction without including any microionic correlations. However, here the mechanism of attraction is related to mathematical artifacts of the linearization itself and does not correspond to a real physical effect. The fact that this prediction is in agreement with the theories beyond the mean-field level is purely accidental and is intrinsically connected with the inadequacy (meaning incorrect application) of the PB mean-field approach at the same limit. In other words, a qualitatively correct result (in this example, attraction) may be deceptively anticipated in the strong-coupling limit because of the simultaneous application of two inadequate approximations, namely, the mean-field PB equation and its subsequent linearization.

The application of the linearization scheme to the exactly solvable planar case sheds light on its limits of applicability. Because the mechanisms of attraction in the planar geometry are already well known, this represents the perfect framework where the linearized theories should be tested. The *a priori* knowledge about the mechanisms of attraction may be used to confirm or invalidate predictions of the linearized approaches. These were mainly applied for deionized aqueous suspensions of charged colloids to theoretically explain the very puzzling—and still controversial—physical phenomenon of gas/liquid-type phase separation mediated by monovalent counterions, see Ref. [9]. In this sense, it would be very instructive if these linearized theories [10] would also be applied to the well-studied planar case. It will not be very surprising if eventually they will yield attraction under the same conditions predicted by the linearization of the PB equation. However, as discussed above, this spurious attraction will have few in common with the real physical mechanism that requires (in the planar case) finite-size effects and microionic correlations. Although important for a correct physical description of the attraction in the planar geometry, the role of the microionic correlations [8] are beyond the scope of the current work.

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APPENDIX A: EXACT NONLINEAR SOLUTION

In this Appendix we review the exact nonlinear PB solution in the traditional gauge $\mu_{\mathrm{el}}=0$ and give the explicit expression of the nonlinear semi-grand-canonical potential Ω. In the standard gauge $\mu_{\mathrm{el}}=0$ [56] the nonlinear problem reduces into solving the usual PB equation for two charged infinite planes [1,3]

$$\frac{d^2\varphi(x)}{dx^2}=\kappa_b^2\sinh\varphi(x)+\frac{2}{\Lambda}[\delta(x+L)+\delta(x-L)],$$

$$n_{\pm}(x)=n_b e^{\mp\varphi(x)}, \tag{A1}$$

with the appropriate boundary conditions

$$\varphi'(x=0)=0 \quad \text{and} \quad \varphi'(x=\mp L)=\pm\frac{2}{\Lambda}, \tag{A2}$$

the prime ($'$) denoting differentiation with respect to the argument. The Debye screening length κ_b^{-1} associated with the bulk density n_b of the infinite salt reservoir and the Gouy-Chapman length Λ were defined in Sec. II by Eqs. (7) and (8), respectively.

Using the mathematical identity $d^2\varphi(x)/dx^2=\frac{1}{2}\,d(\varphi')^2/d\varphi$, it is possible to integrate the nonlinear PB Eq. (A1) exactly,

$$[\varphi'(x)]^2=\kappa_b^2[2\cosh\varphi(x)-2\cosh\varphi_0], \tag{A3}$$

$$\kappa_b|x|=\int_{\varphi(x)}^{\varphi_0}\frac{d\varphi}{\sqrt{2\cosh\varphi-2\cosh\varphi_0}}=\frac{F\left(\arccos\left[\sinh\frac{\varphi_0}{2}\Big/\sinh\frac{\varphi(x)}{2}\right]\,\middle|\,1\Big/\cosh^2\frac{\varphi_0}{2}\right)}{\cosh\frac{\varphi_0}{2}}, \tag{A4}$$

whose solution is written in terms of the midplane electrostatic potential $\varphi_0<0$ and $F(\varphi|m)=\int_0^{\varphi}d\theta/\sqrt{1-m\sin^2\theta}$ is the incomplete elliptic integral of the first kind [57–60]. Applying the boundary conditions (A2) yields

$$\frac{2}{\lambda}=\sqrt{2\cosh\varphi_L-2\cosh\varphi_0}, \tag{A5}$$

$$l=\int_{\varphi_L}^{\varphi_0}\frac{d\varphi}{\sqrt{2\cosh\varphi-2\cosh\varphi_0}}=\frac{F\left(\arccos\left[\sinh\frac{\varphi_0}{2}\Big/\sinh\frac{\varphi_L}{2}\right]\,\middle|\,1\Big/\cosh^2\frac{\varphi_0}{2}\right)}{\cosh\frac{\varphi_0}{2}}, \tag{A6}$$

where we defined the two dimensionless distances $\lambda\equiv\kappa_b\Lambda$ and $l\equiv\kappa_b L$, and $\varphi_L<\varphi_0<0$ is the surface electrostatic potential at the charged planes. Introducing the variable

$$t\equiv\sinh^2\frac{\varphi_0}{2}, \tag{A7}$$

the two boundary conditions can be combined into the eigenvalue equation

$$l\sqrt{1+t}=F\left[\arctan\left(\frac{1}{\lambda\sqrt{t}}\right)\,\middle|\,\frac{1}{1+t}\right]$$

$$\text{or}\quad \lambda\sqrt{t}=\mathrm{cs}\left(l\sqrt{1+t}\,\middle|\,\frac{1}{1+t}\right), \tag{A8}$$

where $\mathrm{cs}(u|m)=\mathrm{cn}(u|m)/\mathrm{sn}(u|m)$ is the ratio of the cosine-amplitude and sine-amplitude Jacobi elliptic functions [57–60]. The explicit exact solution of the nonlinear PB problem can then be written as

$$\varphi(x)=-2\,\mathrm{arcsinh}\left[\sqrt{t}\Big/\mathrm{cn}\left(\kappa_{\mathrm{b}}|x|\sqrt{1+t}\,\middle|\,\frac{1}{1+t}\right)\right],\quad |x|\leqslant L. \tag{A9}$$

It should be remarked that the exact solution to the nonlinear PB problem may be cast in several equivalent forms. Verwey and Overbeek [61], also quoted by Hunter [62], gave an alternative form for the implicit solution (A4),

$$\begin{aligned}\kappa_b|x| &= l+2e^{-\varphi_0/2}[F(\arcsin e^{-(\varphi_L-\varphi_0)/2}|e^{-2\varphi_0})\\ &\quad -F(\arcsin e^{-[\varphi(x)-\varphi_0]/2}|e^{-2\varphi_0})]\\ &= 2e^{-\varphi_0/2}[K(e^{-2\varphi_0})-F(\arcsin e^{-[\varphi(x)-\varphi_0]/2}|e^{-2\varphi_0})],\end{aligned} \tag{A10}$$

where $K(m)=F(\pi/2|\ m)$ is the complete elliptic integral of the first kind [57–60], while Behrens and Borkovec's version [63] to the explicit solution (A9) reads

$$\varphi(x)=\varphi_0+2\ \ln \mathrm{cd}(e^{-\varphi_0/2}\kappa_b|x|/2|e^{2\varphi_0}), \tag{A11}$$

where $\mathrm{cd}(u|m)$ is the cd Jacobi elliptic function [57–60]. However, none of these previous works presented the explicit expression for the nonlinear PB semi-grand-canonical potential $\Omega\equiv\Omega[n_\pm(x)]_{\mathrm{equil}}$, which can be extracted from Ref. [19] by neglecting the electrostatic and elastic contributions arising from the polyelectrolyte brushes.

The dimensionless excess [64] semi-grand-canonical potential per unit area

$$\omega(\lambda,l)\equiv\frac{\kappa_b}{2n_b}\left[\frac{\beta\Omega(\Lambda,L)}{A}+2n_bL\right], \tag{A12}$$

may be evaluated inserting the exact nonlinear solution (A9) into the semi-grand-canonical functional (2) and performing the integrations. Using additionally the relations

$$\cosh\varphi_L=1+2t+\frac{2}{\lambda^2},\quad \cosh\varphi_\infty=1+\frac{2}{\lambda^2}, \tag{A13}$$

where $\varphi_\infty<0$ is the reduced electrostatic surface potential at the charged plane at infinite separation, and the fact that $\varphi_L<0$ and $\varphi_\infty<0$, the excess semi-grand-canonical potential ω may be cast, after some tedious algebra, in the form [65,66]

$$\begin{aligned}\omega(\lambda,l) &= \frac{2}{\lambda}\mathrm{arccosh}\left(1+2t+\frac{2}{\lambda^2}\right)-\frac{4}{\lambda}\sqrt{\frac{1+\lambda^2(1+t)}{1+\lambda^2 t}}\\ &\quad +4\sqrt{1+t}\ \ E\left[\arctan\left(\frac{1}{\lambda\sqrt{t}}\right)\middle|\frac{1}{1+t}\right]-2tl,\end{aligned} \tag{A14}$$

$$\omega(\lambda,\infty)=\frac{2}{\lambda}\mathrm{arccosh}\left(1+\frac{2}{\lambda^2}\right)+4\left(1-\frac{1}{\lambda}\sqrt{1+\lambda^2}\right), \tag{A15}$$

where $E(\varphi|m)=\int_0^\varphi d\theta\sqrt{1-m\sin^2\theta}$ is the incomplete elliptic integral of the second kind [57–60] and $\omega(\lambda,\infty)$ represents the nonlinear excess self-energy of the system at infinite separation.

The osmotic-pressure difference ΔP between the interplane region and the infinite salt reservoir can be written in terms of the midplane reduced electrostatic potential φ_0—which (in general) does not coincide with the arbitrary midplane electrostatic potential ψ_0 in the gauge-invariant formulation, introduced in Eq. (6),

$$\begin{aligned}\Pi &\equiv \frac{\beta\Delta P}{2n_b}=-\frac{1}{2n_b}\frac{d}{dL}\left[\frac{\beta\Omega(\Lambda,L)}{A}+2n_bL\right]_{\mu_\pm}\\ &= -\frac{d\omega(\lambda,l)}{dl}=2\ \sinh^2\frac{\varphi_0}{2}=2t.\end{aligned} \tag{A16}$$

Equation (A16) is a mean-field version [67] of the boundary-density theorem, which states that the osmotic pressure is simply given by the sum of the microionic densities at the midplane (WS cell boundary). This simple relation does not hold beyond the mean-field level because of finite ionic-size effects and the presence of microionic correlations between particles located in the different semispaces separated by the midplane—even though it still does for *one* charged plane with the electrolyte confined by a *neutral* midplane [68]. We restrict ourselves, however, to the nonlinear mean-field result (A16), which clearly predicts that the osmotic-pressure difference Π *is always positive.* The osmotic-pressure difference (A16), written in the standard gauge $\mu_{\mathrm{el}}=0$, is equivalent to the gauge-invariant form presented in the main text, Eq. (6). Although Eq. (A16) looks much simpler than Eq. (6), it is not suitable for a direct comparison with its linearized counterpart (22).

APPENDIX B: EXACT NONLINEAR AVERAGED DENSITIES

In this Appendix we will compare the uniform expansion densities about which the linearization is performed—the state-independent zeroth order Donnan densities $c_\pm^{(1)}$, Eqs. (9)—with the exact nonlinear PB averages $c_\pm$, Eqs. (11).

By using the definite integrals

$$\int_{\varphi_L}^{\varphi_0}\frac{d\varphi\sinh\varphi}{\sqrt{2\cosh\varphi-2\cosh\varphi_0}}=-\sqrt{2\cosh\varphi_L-2\cosh\varphi_0}, \tag{B1}$$

$$\begin{aligned}&\int_{\varphi_L}^{\varphi_0}\frac{d\varphi\cosh\varphi}{\sqrt{2\cosh\varphi-2\cosh\varphi_0}}\\ &\quad =\frac{\cosh\varphi_0}{\cosh\frac{\varphi_0}{2}}\ F\left(\arccos\left[\sinh\frac{\varphi_0}{2}\Big/\sinh\frac{\varphi_L}{2}\right]\middle|1/\cosh^2\frac{\varphi_0}{2}\right)\\ &\qquad -2\cosh\frac{\varphi_0}{2}\\ &\qquad \times E\left(\arccos\left[\sinh\frac{\varphi_0}{2}\Big/\sinh\frac{\varphi_L}{2}\right]\middle|1/\cosh^2\frac{\varphi_0}{2}\right)\\ &\qquad -\coth\frac{\varphi_L}{2}\sqrt{2\cosh\varphi_L-2\cosh\varphi_0},\end{aligned} \tag{B2}$$

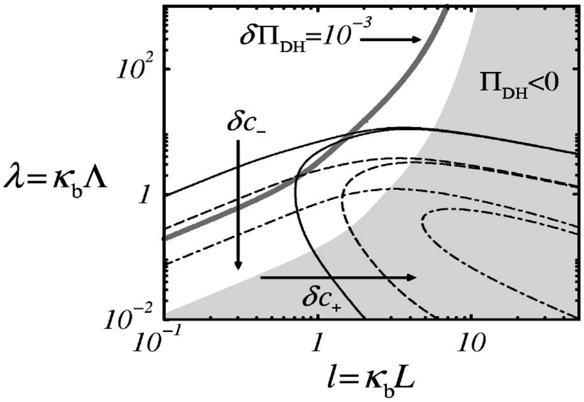

FIG. 3. Deviations from the PB averaged densities of the state-independent zeroth order Donnan densities, which were used to perform the quadratic expansions of the nonlinear functional. The arrows indicate the direction of increasing logarithmic deviations $\delta c_\pm$ from the PB results: 10^{-3} (solid lines), 10^{-2} (dashed lines), and 10^{-1} (dot-dashed lines). To allow a comparison with the region where the linearized theory breaks down, we also plotted the locus (dark gray thick line) where the logarithmic deviation from PB of the linearized osmotic-pressure difference is $\delta\Pi_{\rm DH}=10^{-3}$. In the light gray region the linearized osmotic-pressure difference becomes negative, $\Pi_{\rm DH}<0$. Although there is a close connection between this region and the increase of the deviations $\delta c_\pm$ for high-surface charges ($\lambda\ll 1$), for low-surface charges ($\lambda\gg 1$) and large separations ($l\gg 1$), the linearized theory still predicts a negative linearized osmotic-pressure difference (upper-right region), while the full nonlinear one vanishes exponentially from positive values.

it is possible to obtain the exact nonlinear PB averaged densities

$$\frac{c_\pm}{n_b}\equiv\langle e^{\mp\varphi(x)}\rangle=\sqrt{\left(\frac{2}{\lambda l}\right)^2+\langle e^{\varphi(x)}\rangle\langle e^{-\varphi(x)}\rangle}\pm\frac{2}{\lambda l}$$
$$=1+2t\pm\frac{2}{\lambda l}-\frac{2}{l}\sqrt{1+t}\;E\left[\arctan\left(\frac{1}{\lambda\sqrt{t}}\right)\middle|\frac{1}{1+t}\right]$$
$$+\frac{2}{\lambda l}\sqrt{\frac{1+\lambda^2(1+t)}{1+\lambda^2 t}}. \tag{B3}$$

In Fig. 3 we compare them with the uniform densities about which the linearization is performed, the state-independent zeroth order Donnan densities (9)

$$\frac{c_\pm^{(1)}}{n_b}=\sqrt{\left(\frac{2}{\lambda l}\right)^2+1}\pm\frac{2}{\lambda l}, \tag{B4}$$

by looking at their logarithmic deviations from the corresponding exact PB averages

$$\delta c_\pm\equiv\ln c_\pm-\ln c_\pm^{(1)}. \tag{B5}$$

APPENDIX C: EXTENDED EXPANSIONS OF THE NONLINEAR SOLUTION

In this Appendix we present extended expansions of the nonlinear semi-grand-canonical potential and of the nonlinear osmotic-pressure difference that are valid in the region where the linearization breaks down. We have made extensive use of Refs. [57–60] throughout this Appendix.

1. Extended Gouy-Chapman limit

Both the counterionic ideal-gas (finite λ) as well as the Gouy-Chapman (λ→0) asymptotics of the nonlinear osmotic-pressure difference, Eqs. (29) and (32), respectively, were obtained in the small-separation ($l\to 0$) limit. In fact, for any ratio $\xi=\lambda/l$ the summation over the λ/l series for the leading terms up to $O(l^2)$ may be performed exactly, yielding

$$t=\left(\frac{y}{l}\right)^2-\frac{1}{2}+\frac{3(1+\xi+\xi^2y^2)(1+\xi^2y^2)+2\xi^3y^2}{32y^2(1+\xi+\xi^2y^2)(1+\xi^2y^2)}\;l^2$$
$$+O(l^4), \tag{C1}$$

where $y=y(\xi)$ is the solution of the transcendental equation

$$\xi y\tan y=1. \tag{C2}$$

This general expression yields the leading term $O(l^{-2})$ of the counterionic ideal-gas (finite λ, when $y\to\sqrt{l/\lambda}\to 0$), Eq. (29), as well as the Gouy-Chapman (high-surface charge, when $\lambda\to 0$, $y\to\pi/2$), Eq. (32), asymptotics as special cases. The excess semi-grand-canonical potential ω may be obtained by integration of the osmotic-pressure difference $2t$, leading to

$$\omega(\lambda,l)=\frac{2y^2}{l}-\frac{4}{\lambda}\left[1+\ln\left(\frac{\lambda}{2}\sin y\right)\right]+l$$
$$-\frac{1}{2}\cot y\left(\sin^2 y+\frac{l}{\lambda}\right)\left(\frac{l}{2y}\right)^3+O(l^5). \tag{C3}$$

While the third and fourth terms are the leading corrections due to the presence of salt, the two first terms can be related to half of the *exact nonlinear* Helmholtz free energy of two charged infinite planes in the presence of neutralizing counterions only (salt-free Gouy-Chapman case),

$$\frac{\beta F}{A}=\frac{1}{4\pi l_B}\left\{\frac{2y^2}{L}-\frac{4}{\Lambda}\left[1+\ln(\Lambda\sin y)+\frac{1}{2}\ln\left(\frac{2\pi l_B}{\zeta_+^3}\right)\right]\right\}, \tag{C4}$$

where y is the solution of the transcendental equation $y\tan y=L/\Lambda$.

We define the extended Gouy-Chapman limit by truncating the above expansions, neglecting thus higher-order terms,

$$\omega_{\mathrm{GC}}(\lambda,l)\equiv\frac{2y^2}{l}-\frac{4}{\lambda}\left[1+\ln\left(\frac{\lambda}{2}\sin y\right)\right]+l-\frac{1}{2}\cot y\left(\sin^2 y+\frac{l}{\lambda}\right)\left(\frac{l}{2y}\right)^3, \tag{C5}$$

$$\Pi_{\mathrm{GC}}(\lambda,l)\equiv 2\left(\frac{y}{l}\right)^2-1+\frac{3(1+\xi+\xi^2y^2)(1+\xi^2y^2)+2\xi^3y^2}{16y^2(1+\xi+\xi^2y^2)(1+\xi^2y^2)}l^2, \tag{C6}$$

where $y=y(\xi)$ is the solution of the transcendental equation (C2).

2. Extended large-separation limit

The large-separation osmotic-pressure asymptotics, Eq. (35), displays oscillations in the crossover ($l\approx 1$) region, even by taking higher-order terms into account. Because we want to match the linearized DH-like, the extended Gouy-Chapman and the large-separation asymptotic expressions at the crossover region, we need to find an extended expansion that does not display this shortcoming. In fact the pressure oscillations are avoided if one uses instead the implicit form $l=l(\lambda,m)$, which is obtained by expanding the eigenvalue equation

$$l(\lambda,m)=\sqrt{m}\,K(m)-\sqrt{m}\,F[\arctan(\lambda/\sqrt{m})|m], \tag{C7}$$

in powers of $(1-m)\equiv t/(1+t)$. Accurate results in the crossover region, which will cover almost the whole ($l\times\lambda$) parameter space with logarithmic pressure deviations from the exact PB within 0.1%, are obtained by truncating the expansions of the elliptic integrals [69] up to fourth-order about $m=1$,

$$\begin{aligned}\frac{l(\lambda,m)}{\sqrt{m}}={}&\ln 4-\frac{1}{2}\ln(1-m)+\frac{1}{4}(1-m)\left[\ln 4-1-\frac{1}{2}\ln(1-m)\right]+\frac{3}{128}(1-m)^2[6\ln 4-7-3\ln(1-m)]\\&+\frac{5}{1536}(1-m)^3[30\ln 4-37-15\ln(1-m)]+\frac{35}{196608}(1-m)^4[420\ln 4-533-210\ln(1-m)]\\&-\frac{\lambda(1-m)}{2(1+\lambda^2)^{7/2}}\left[(1+\lambda^2)^3+\frac{1}{4}(1-m)(1+\lambda^2)^2(3-2\lambda^4)+\frac{1}{24}(1-m)^2(1+\lambda^2)(15+5\lambda^2-10\lambda^4+6\lambda^6+9\lambda^8)\right.\\&\left.+\frac{1}{192}(1-m)^3(105+70\lambda^2-70\lambda^4+28\lambda^6+66\lambda^8-72\lambda^{10}-60\lambda^{12})\right]-\ln(\lambda+\sqrt{1+\lambda^2})-\frac{1-m}{4}[\ln(\lambda+\sqrt{1+\lambda^2})\\&-\lambda\sqrt{1+\lambda^2}]-\frac{3(1-m)^2}{64}[3\ln(\lambda+\sqrt{1+\lambda^2})-\lambda\sqrt{1+\lambda^2}(3-2\lambda^2)]-\frac{5(1-m)^3}{768}[15\ln(\lambda+\sqrt{1+\lambda^2})\\&-\lambda\sqrt{1+\lambda^2}(15-10\lambda^2+8\lambda^4)]-\frac{35(1-m)^4}{49152}[105\ln(\lambda+\sqrt{1+\lambda^2})-\lambda\sqrt{1+\lambda^2}(105-70\lambda^2+56\lambda^4-48\lambda^6)].\end{aligned} \tag{C8}$$

The extended large-separation osmotic-pressure difference $\Pi_{\mathrm{LS}}\equiv 2(1-m)/m$ is defined implicitly by the above relation.

The associated semi-grand-canonical potential is obtained by truncating the expansion of the asymptotic large-separation ($l\to\infty$) excess semi-grand-canonical potential, evaluated by integration of the osmotic-pressure difference, $2t=-d\omega/dl$,

$$\omega_{\mathrm{LS}}(\lambda,l)\equiv\frac{2}{\lambda}\operatorname{arccosh}\left(1+\frac{2}{\lambda^2}\right)+4\left(1-\frac{1}{\lambda}\sqrt{1+\lambda^2}\right)-\frac{2}{m}(1-m)l(\lambda,m)-2\int_1^m\frac{d\mu}{\mu^2}\,l(\lambda,\mu). \tag{C9}$$

This final expression can be straightforwardly casted in an explicit form by evaluating integrals of type $\int_1^m d\mu(1-\mu)^n/\mu^{3/2}, \int_1^m d\mu \ln(1-\mu)(1-\mu)^n/\mu^{3/2}$, for $n=0,\dots,4$.

APPENDIX D: ENSEMBLE-INVARIANT SELF-CONSISTENT LINEARIZED EQUATIONS

In this Appendix we show that the linearized equations that preserve the ensemble invariance do not lead to any improvements in the agreement between the linearized and nonlinear osmotic pressures in comparison to the linearized versions obtained in Sec. III.

As discussed in detail in Appendix G of Ref. [9], the linearized semi-grand-canonical equations of state may be rendered *ensemble invariant* if—instead of using the state-independent zeroth order Donnan densities $c_\pm^{(1)}$, Eqs. (9)—one uses the quadratic truncation of the nonlinear averages $c_\pm = c_\pm^{(2)} + O[\langle \delta_3(x)\rangle]$,

$$c_\pm^{(2)} \equiv \frac{\sqrt{n_c^2+(2n_b)^2 e^{\langle \delta_2(x)\rangle}} \pm n_c}{2}, \tag{D1}$$

as expansion densities to obtain the linearized semi-grand-canonical functional. With the inclusion of the quadratic state-dependent contribution $\langle \delta_2(x)\rangle$ to the average densities, we obtain the ensemble-invariant self-consistent linearized semi-grand-canonical potential and linearized osmotic-pressure difference

$$\begin{aligned}\hat{\omega}_{\mathrm{DH}}(\lambda,l) &\equiv \frac{\kappa_b}{2n_b}\left[\frac{\beta\hat{\Omega}_{\mathrm{DH}}(\Lambda,L)}{A}+2n_bL\right]\\ &= \frac{2}{\lambda}\left[\operatorname{arctanh}\hat{\eta} - \frac{1}{\hat{\eta}} + \frac{1}{2}\hat{\eta}\hat{k}l\mathcal{L}(\hat{k}l)\right.\\ &\qquad \left. + \frac{1}{2\hat{\eta}}\langle \delta_2(x)\rangle\right] + l\\ &= \frac{2}{\lambda}\left\{\operatorname{arctanh}\hat{\eta} - \frac{1}{\hat{\eta}} + \frac{5}{4}\hat{\eta}\hat{k}l\mathcal{L}(\hat{k}l)\right.\\ &\qquad \left. + \frac{1}{4}\,\hat{\eta}(\hat{k}l)^2[\mathcal{L}^2(\hat{k}l)-1]\right\} + l,\end{aligned} \tag{D2}$$

$$\begin{aligned}\hat{\Pi}_{\mathrm{DH}}(\lambda,l) &\equiv -\frac{d\hat{\omega}_{\mathrm{DH}}(\lambda,l)}{dl}\\ &= \hat{k}^2\left[1+\hat{\eta}\delta_1(0)+\frac{1}{2}\delta_2(0)-\frac{1}{2}\langle \delta_2(x)\rangle\right]-1\\ &= \hat{k}^2\left\{1+\frac{1}{4}\hat{\eta}^2\hat{k}l\mathcal{L}(\hat{k}l)\right.\\ &\qquad \left. + \frac{1}{4}(\hat{\eta}\hat{k}l)^2[\mathcal{L}^2(\hat{k}l)-1]\right\}-1,\end{aligned} \tag{D3}$$

where the dimensionless parameters

$$\hat{\eta} = \frac{1}{\sqrt{1+(\lambda l/2)^2 e^{\langle \delta_2(x)\rangle}}},$$

$$\hat{k}^2 = \sqrt{e^{\langle \delta_2(x)\rangle}+[2/(\lambda l)]^2} = \frac{e^{\langle \delta_2(x)\rangle/2}}{\sqrt{1-\hat{\eta}^2}}, \tag{D4}$$

are given implicitly in terms of the quadratic moment of the electrostatic potential

$$\langle \delta_2(x)\rangle = \frac{1}{2}\hat{\eta}^2\hat{k}l\{3\mathcal{L}(\hat{k}l)+\hat{k}l[\mathcal{L}^2(\hat{k}l)-1]\}. \tag{D5}$$

To compute the ensemble-invariant linearized osmotic-pressure difference $\hat{\Pi}_{\mathrm{DH}}$, Eq. (D3), one needs to take into account the total derivatives of the parametric forms, Eqs. (D4),

$$\begin{aligned}\frac{d}{dl} &= \frac{\partial}{\partial l} + \frac{d\hat{\eta}}{dl}\,\frac{\partial}{\partial\hat{\eta}} + \frac{d\hat{k}}{dl}\,\frac{\partial}{\partial\hat{k}}\\ &= \frac{\partial}{\partial l} - \frac{\hat{\eta}}{l}(1-\hat{\eta}^2)\left(1+\frac{l}{2}\,\frac{d\langle \delta_2(x)\rangle}{dl}\right)\frac{\partial}{\partial\hat{\eta}}\\ &\quad - \frac{\hat{k}\hat{\eta}^2}{2l}\left[1-\frac{l}{2}\left(\frac{1-\hat{\eta}^2}{\hat{\eta}^2}\right)\frac{d\langle \delta_2(x)\rangle}{dl}\right]\frac{\partial}{\partial\hat{k}}.\end{aligned} \tag{D6}$$

In accordance to the infinite-separation linearized self-energy obtained in Sec. III, the ensemble-invariant version is also given by $\hat{\omega}_{\mathrm{DH}}(\lambda, l\to\infty)=2/\lambda^2$.

In Figs. 1 and 2 we compare the two linearized osmotic-pressure definitions Π_{DH} and $\hat{\Pi}_{\mathrm{DH}}$, given by Eqs. (21) and (D3), with the exact nonlinear version Π, given by Eq. (A16). The dotted lines in Figs. 1 and 2 *suggest* a better agreement between the ensemble-invariant linearized osmotic-pressure difference $\hat{\Pi}_{\mathrm{DH}}$ and the full nonlinear counterpart Π—in comparison to the linearized version Π_{DH}, obtained in Sec. III, which is not ensemble invariant. However, as shown below by explicit analytical comparison, these numerical evidences are in fact misleading.

Asymptotic analytical expansions of the ensemble-invariant linearized osmotic-pressure difference $\hat{\Pi}_{\mathrm{DH}}$ about the weak coupling ($l_B\to 0$)

$$\begin{aligned}\hat{\Pi}_{\mathrm{DH}} &= \Pi_{\mathrm{DH}} + k^2\left[\frac{\eta^4}{16200}(\eta^2+5)(1-\eta^2)k^8l^8+O(k^{10}l^{10})\right]\\ &= k^2\left[1-\frac{\eta^2}{6}k^2l^2-\frac{\eta^2}{90}(\eta^2-3)k^4l^4+\frac{\eta^2}{945}(2\eta^2-5)k^6l^6\right.\\ &\quad \left. -\frac{\eta^2}{113400}(7\eta^6+28\eta^4+\eta^2-84)k^8l^8+O(k^{10}l^{10})\right]\\ &\quad -1,\end{aligned} \tag{D7}$$

and the counterionic ideal-gas ($L\to 0$, finite Λ) limits

$$\hat{\Pi}_{\rm DH} = \Pi_{\rm DH} + \frac{2}{\lambda l}\left\{ \frac{\lambda^4}{675}\left(\frac{l}{\lambda}\right)^6 + O[(l/\lambda)^7] \right\}, \qquad \text{(D8)}$$

show explicitly that both linearized osmotic pressures, $\Pi_{\rm DH}$ and $\hat{\Pi}_{\rm DH}$, agree with the full nonlinear PB version Π up to the *same order*—cf. Eqs. (26)–(31). Therefore, the numerical indications of a better agreement of $\hat{\Pi}_{\rm DH}$, as suggested by Figs. 1 and 2, are purely fortuitous. In fact, for ratios $\Lambda/L > 10^2$ (beyond the values shown in Fig. 2) one observes a crossover between the deviations of the linearized versions, $\Pi_{\rm DH}$ and $\hat{\Pi}_{\rm DH}$, with respect to the full nonlinear osmotic-pressure difference Π. These results, however, can only be verified *a posteriori*.

[1] J. N. Israelachvili, *Intermolecular and Surface Forces,* 2nd ed. (Academic Press, London, 1992).

[2] S. A. Safran, *Statistical Thermodynamics of Surfaces, Interfaces and Membranes* (Addison-Wesley, Reading, MA, 1994).

[3] D. Andelman, in *Handbook of Biological Physics,* edited by R. Lipowsky and E. Sackmann (Elsevier, Amsterdam, 1995), Vol. 1B, Chap. 12.

[4] R. R. Netz and H. Orland, Eur. Phys. J. E **1**, 203 (2000).

[5] M. Deserno and C. Holm, in *Proceedings of the NATO Advanced Study Institute on Electrostatic Effects in Soft Matter and Biophysics,* edited by C. Holm, P. Kékicheff, and R. Podgornik (Kluwer, Dordrecht, 2001), p. 27.

[6] G. M. Torrie and J. P. Valleau, Chem. Phys. Lett. **65**, 343 (1979); J. Chem. Phys. **73**, 5807 (1980); B. Jönsson, H. Wennerström, and B. Halle, J. Phys. Chem. **84**, 2179 (1980); W. van Megen and I. Snook, J. Chem. Phys. **73**, 4656 (1980); A. G. Moreira and R. R. Netz, Eur. Phys. J. E **8**, 33 (2002).

[7] H. L. Friedman and W. D. T. Dale, in *Statistical Mechanics, Part A: Equilibrium Techniques,* edited by B. J. Berne (Plenum, New York, 1977), Chap. 3, p. 85.

[8] Y. Levin, Rep. Prog. Phys. **65**, 1577 (2002).

[9] M. N. Tamashiro and H. Schiessel, J. Chem. Phys. **119**, 1855 (2003).

[10] R. van Roij and J.-P. Hansen, Phys. Rev. Lett. **79**, 3082 (1997); R. van Roij, M. Dijkstra, and J.-P. Hansen, Phys. Rev. E **59**, 2010 (1999); A. R. Denton, *ibid.* **62**, 3855 (2000); P. B. Warren, J. Chem. Phys. **112**, 4683 (2000); D. Y. C. Chan, P. Linse, and S. N. Petris, Langmuir **17**, 4202 (2001); S. N. Petris and D. Y. C. Chan, J. Chem. Phys. **116**, 8588 (2002); L. B. Bhuiyan and C. W. Outhwaite, *ibid.* **116**, 2650 (2002).

[11] A. Diehl, M. C. Barbosa, and Y. Levin, Europhys. Lett. **53**, 86 (2001).

[12] H. H. von Grünberg, R. van Roij, and G. Klein, Europhys. Lett. **55**, 580 (2001).

[13] M. Deserno and H. H. von Grünberg, Phys. Rev. E **66**, 011401 (2002).

[14] F. G. Donnan, Chem. Rev. **1**, 73 (1924).

[15] J. Th. G. Overbeek, Prog. Biophys. Biophys. Chem. **6**, 57 (1956).

[16] T. L. Hill, Discuss. Faraday Soc. **21**, 31 (1956); J. Phys. Chem. **61**, 548 (1957).

[17] V. Reus, L. Belloni, T. Zemb, N. Lutterbach, and H. Versmold, J. Phys. II **7**, 603 (1997).

[18] M. N. Tamashiro, Y. Levin, and M. C. Barbosa, Eur. Phys. J. B **1**, 337 (1998).

[19] M. N. Tamashiro, E. Hernández-Zapata, P. A. Schorr, M. Balastre, M. Tirrell, and P. Pincus, J. Chem. Phys. **115**, 1960 (2001).

[20] B. V. Derjaguin, Kolloid-Z. **69**, 155 (1934).

[21] L. R. White, J. Colloid Interface Sci. **95**, 286 (1983).

[22] P. Pincus, J.-F. Joanny, and D. Andelman, Europhys. Lett. **11**, 763 (1990).

[23] Strictly speaking, we should say explicitly gauge invariant—instead of simply gauge invariant—because all consistent theories should be automatically gauge invariant. This is, of course, the case of the standard solution of the nonlinear PB equation in the particular gauge $\mu_{\rm el}=0$ presented in Appendix A. Even though it is nontrivial to see the gauge invariance of the nonlinear equations by changes in the electrostatic potential $\varphi(x) \to \varphi(x) + \phi$, where ϕ is an arbitrary constant, it must indeed be gauge invariant. In the standard nonlinear solution there is an unfortunate coupling between the charge-neutrality constraint and the choice of gauge, which might lead to confusion.

[24] The Boltzmann-weighted equilibrium profiles (4) describe the ionic densities between the two charged plates. They do not apply to the infinite reservoir, that is only characterized by their associated (mean-field) ideal-gas microion chemical potentials $\beta\mu_{\pm} = \ln(n_b \zeta_{\pm}^3)$. The equilibrium density profiles (4) were constructed in such a way to obey the charge-neutrality constraint (3), which implies an excess of counterions in the interplane region to neutralize the negative charge of the plates. This counterion excess is absent in the infinite salt reservoir. See also Appendixes E and F of Ref. [9] for an explanation of the distinct roles attributed to the Lagrange multiplier $\mu_{\rm el}$ and the microion chemical potentials $\mu_{\pm}$, which are associated to different physical constraints of the problem, namely, the overall charge-neutrality constraint (3) and the electrochemical equilibrium with the infinite salt reservoir of bulk density n_b.

[25] G. Gouy, J. Phys. (Paris) **9**, 457 (1910).

[26] D. L. Chapman, Philos. Mag. **25**, 475 (1913).

[27] E. Trizac and J.-P. Hansen, Phys. Rev. E **56**, 3137 (1997).

[28] The nomenclature DH equation for the linearized PB equation may be somewhat misleading, since it is obtained by a linearization of the mean-field PB functional, which does not include any microion-microion (neither in the interplane region nor in the infinite reservoir) correlations. The original DH theory for symmetric electrolytes [8,29–31] takes these correlations automatically into account and leads to the famous electrostatic osmotic-pressure limiting law $-\kappa^3/(24\pi)$. A more appropriate interpretation of the linearized PB (DH-like) equation is that it corresponds to an expansion about the infinite-temperature limit of the mean-field nonlinear PB equation.

[29] P. W. Debye and E. Hückel, Phys. Z. **24**, 185 (1923).

[30] T. L. Hill, *An Introduction to Statistical Thermodynamics* (Dover, New York, 1986).

[31] D. A. McQuarrie, *Statistical Mechanics* (Harper-Collins, New York, 1976).

[32] The asymptotic expansions of the full nonlinear PB osmotic-pressure difference Π—given by Eqs. (26), (29), (32), and (35)—provide higher-order terms and extend previous calculations by Pincus *et al.* [3,22] being in agreement with them except for the so-called Debye-Hückel region. In our notation, their osmotic-pressure asymptotic expressions for the different regimes read as follows. Counterionic ideal gas: $\Pi = 2/(\lambda l)$; Gouy-Chapman: $\Pi = (\pi/l)^2/2$; intermediate $(l \to \infty, \lambda \to 0)$: $\Pi = 32 e^{-2l}$; Debye-Hückel $(l \to \infty, \lambda \neq 0)$: $\Pi = 2/(\lambda \sinh l)^2$. The two latter regimes are covered by the large-separation limit (35).

[33] L. Guldbrand, B. Jönsson, H. Wennerström, and P. Linse, J. Chem. Phys. **80**, 2221 (1984).

[34] M. J. Stevens and M. O. Robbins, Europhys. Lett. **12**, 81 (1990).

[35] A. Diehl, M. N. Tamashiro, M. C. Barbosa, and Y. Levin, Physica A **274**, 433 (1999).

[36] R. Kjellander and D. J. Mitchell, Chem. Phys. Lett. **200**, 76 (1992); R. Kjellander, Ref. [5], p. 317.

[37] M. Lozada-Cassou, W. Olivares, and B. Sulbarán, Phys. Rev. E **53**, 522 (1996).

[38] I. Rouzina and V. A. Bloomfield, J. Phys. Chem. **100**, 9977 (1996).

[39] B. I. Shklovskii, Phys. Rev. E **60**, 5802 (1999).

[40] P. A. Pincus and S. A. Safran, Europhys. Lett. **42**, 103 (1998).

[41] A. W. C. Lau, D. Levine, and P. Pincus, Phys. Rev. Lett. **84**, 4116 (2000); A. W. C. Lau, P. Pincus, D. Levine, and H. A. Fertig, Phys. Rev. E **63**, 051604 (2001); A. W. C. Lau, D. B. Lukatsky, P. Pincus, and S. A. Safran, *ibid.* **65**, 051502 (2002); A. W. C. Lau and P. Pincus, *ibid.* **66**, 041501 (2002).

[42] B.-Y. Ha, Phys. Rev. E **64**, 031507 (2001).

[43] M. N. Tamashiro and P. Pincus, Phys. Rev. E **60**, 6549 (1999).

[44] Y. Burak and D. Andelman, J. Chem. Phys. **114**, 3271 (2001).

[45] A. G. Moreira and R. R. Netz, Europhys. Lett. **52**, 705 (2000); Phys. Rev. Lett. **87**, 078301 (2001); R. R. Netz, Eur. Phys. J. E **5**, 557 (2001).

[46] N. Grønbech-Jensen, R. J. Mashl, R. F. Bruinsma, and W. M. Gelbart, Phys. Rev. Lett. **78**, 2477 (1997).

[47] R. Podgornik and V. A. Parsegian, Phys. Rev. Lett. **80**, 1560 (1998).

[48] B.-Y. Ha and A. J. Liu, Phys. Rev. Lett. **79**, 1289 (1997); **83**, 2681 (1999); Y. Levin, J. J. Arenzon, and J. F. Stilck, *ibid.* **83**, 2680 (1999).

[49] J. J. Arenzon, J. F. Stilck, and Y. Levin, Eur. Phys. J. B **12**, 79 (1999).

[50] F. J. Solis and M. Olvera de la Cruz, Phys. Rev. E **60**, 4496 (1999).

[51] B. I. Shklovskii, Phys. Rev. Lett. **82**, 3268 (1999).

[52] J. J. Arenzon, Y. Levin, and J. F. Stilck, Physica A **283**, 1 (2000).

[53] A. Diehl, H. A. Carmona, and Y. Levin, Phys. Rev. E **64**, 011804 (2001).

[54] J. F. Stilck, Y. Levin, and J. J. Arenzon, J. Stat. Phys. **106**, 287 (2002).

[55] M. Deserno, A. Arnold, and C. Holm, Macromolecules **36**, 249 (2003).

[56] Because of the frequent use of the standard gauge $(\mu_{\mathrm{el}} \equiv 0)$ the fact that this system constitutes a Donnan equilibrium problem has not been emphasized.

[57] *Higher Transcendental Functions,* Bateman Manuscript Project, edited by A. Erdélyi, W. Magnus, F. Oberhettinger, and F. G. Tricomi (McGraw-Hill, New York, 1953), Vol. II.

[58] *Handbook of Mathematical Functions,* edited by M. Abramowitz and I. A. Stegun (Dover, New York, 1970).

[59] P. F. Byrd and M. D. Friedman, *Handbook of Elliptic Integrals for Engineers and Scientists,* 2nd ed. (Springer-Verlag, Berlin, 1971).

[60] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products,* 5th ed., edited by Alan Jeffrey (Academic Press, San Diego, 1994).

[61] E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Dover, New York, 1999), Chap. IV, p. 69.

[62] R. J. Hunter, *Foundations of Colloid Science* (Clarendon Press, Oxford, 1987), Vol. I, problem 7.3.10.

[63] S. H. Behrens and M. Borkovec, Phys. Rev. E **60**, 7040 (1999).

[64] We added a term $2 n_b L$ to $\beta\Omega/A$, which subtracts out the contribution from the infinite reservoir to the semi-grand-canonical potential—leading to a finite excess potential ω at infinite separation. Therefore the osmotic-pressure difference between the interplane region and the salt reservoir is automatically obtained by taking the derivative of the excess semi-grand-canonical potential with respect to the semi-separation L between the charged planes, see Eq. (A16).

[65] As already pointed out in the Introduction, besides its intrinsic relevance, the semi-grand-canonical potential for the planar case has also an important application: by using the Derjaguin approximation [1,20,21], valid when the range of interactions [66] (of order κ_b^{-1}) and the separation distance $2L$ between the two curved surfaces are much smaller than their curvature radius a, it is possible to determine their normal force (per unit area) $\mathcal{F}$ at separation $2L$ by $(1/\kappa_b a)\mathcal{F}(2L) = (k_B T/l_B)[\omega(\lambda, l) - \omega(\lambda, \infty)]$.

[66] Although the bare Coulomb interaction is long-ranged, even deionized aqueous suspensions at neutral pH characterized by small ionic strengths, $n_b \approx 10^{-7}$ M, leads to Debye screening lengths of order $\kappa_b^{-1} \approx 1\ \mu\mathrm{m} \ll a$. Therefore, for surfaces with curvatures of macroscopic size the applicability of the Derjaguin approximation is still valid.

[67] R. A. Marcus, J. Chem. Phys. **23**, 1057 (1955).

[68] H. Wennerström, B. Jönsson, and P. Linse, J. Chem. Phys. **76**, 4665 (1982).

[69] This expansion is nontrivial because algebraic-manipulation computer programs, such as MATHEMATICA and MAPLE, unfortunately do not perform series of the incomplete elliptic integral of the first kind $F(\varphi|m)$ with respect to the second argument m.