Description beyond the mean-field approximation of an electrolyte confined between two planar metallic electrodes

Gabriel Téllez*

Departamento de Física, Universidad de Los Andes, A.A. 4976, Bogotá, Colombia
(Received 23 January 2004; published 30 July 2004)

We study an electrolyte confined in a slab of width W composed of two grounded metallic parallel electrodes. We develop a description of this system in a low coupling regime beyond the mean-field (Poisson–Boltzmann) approximation. There are two ways to model the metallic boundaries: as ideal conductors in which the electric potential is zero, and it does not fluctuate, or as good conductors in which the average electric potential is zero but the thermal fluctuations of the potential are not zero. This latter model is more realistic. For the ideal conductor model we find that the disjoining pressure is positive behaves as $1/W^3$ for large separations with a prefactor that is universal, i.e., independent of the microscopic constitution of the system. For the good conductor boundaries, the disjoining pressure is negative and it has an exponential decay for large W. We also compute the density and electric potential profiles inside the electrolyte. These are the same in both models. If the electrolyte is charge asymmetric, we find that the system is not locally neutral and that a nonzero potential difference builds up between any electrode and the interior of the system although both electrodes are grounded.

I. INTRODUCTION

In this paper, we study an electrolyte solution confined between two parallel planar metallic electrodes. The study of the electrical double layer near an electrode and more generally near any object submerged in an electrolyte is of crucial importance in chemical physics and in colloidal science. This problem was first considered by Gouy [1] and independently by Chapman [2] almost a century ago. Their work is part of the foundations of colloidal science [3] and the physics of electrolytes [4].

However, their work and subsequent developments are based on a mean-field description: the Poisson-Boltzmann equation. Although this mean-field approach describes accurately several properties of the systems, in some situations it misses some subtle effects due to correlations. As an example, we can mention the old controversy about the possibility of attraction between like-charged colloids [3,5] recently renewed by some experimental results [6–8]. It has been shown [9–12] that the mean-field approach (actually any local density approximation) cannot predict any attractive effective interaction. Therefore, the study of electrolyte suspensions beyond the mean-field approximation is important.

This paper is oriented in that sense, although we will not consider here the problem of like-charged attraction between colloids, but the study of an electrolyte solution confined between two parallel metallic planar electrodes beyond the mean-field approximation. We will be interested in questions such as what force is exerted on the planar electrodes, is it attractive or repulsive, etc. To have a clear picture of the role of the correlations in this problem, we will consider the case when the two electrodes are grounded. The mean-field pic-

ture in this case is very simple: the mean-field potential in the electrolyte is zero everywhere and the fluid is uniform and locally neutral. We will describe the first fluctuations around this mean-field picture in a low coupling regime where the average Coulombic energy of the micro-ions of the solution is much smaller than their thermal energy.

We should mention that this same problem was recently considered in Ref. [13]. However, the authors of Ref. [13] made a mistake that has lead them to the wrong conclusions, as explained below. The electrolyte is confined between two conductor parallel planes. Each particle polarizes the planes. There is an interaction energy between each particle and the polarization charge that it induces in the electrodes. In Ref. [13], the authors forgot to include this energy in the Hamiltonian, and this error made most of their conclusions incorrect.

The outline of this paper and our main results can be summarized as follows. In Sec. II, we present the models under consideration and explain the method [14] used to find the thermodynamic properties of the system. Actually, there are two ways to model the metallic electrodes. In a first model, the boundaries are supposed to be made of an ideal conductor material. This model is very simple, but it has the defect of neglecting the fluctuations of the electric potential in the electrodes. In the second model, which is more realistic, the electrodes are supposed to be genuine Coulombic systems with very good conducting properties. We will call this model the good conductor model. In this model, the screening length vanishes inside the conducting electrodes, the average electric potential is zero in the electrodes, but the electric potential can fluctuate. We will obtain results for both models and compare them using results from Ref. [15].

In Sec. III, we compute the grand potential of the system and the pressure. For the ideal conductor model we find that the disjoining pressure is positive. For large separations W of the slab, the disjoining pressure behaves as $1/W^3$. On the

---

*Electronic address: gtellez@uniandes.edu.co

other hand, for the good conductor model, the disjoining pressure turns out to be negative and it decays as $e^{-2\kappa W}$ for large separations, with κ the inverse Debye length.

Finally, in Sec. IV, we find the micro-ion density profiles and the electric potential inside the electrolyte. These quantities are the same regardless of the model used to describe the electrodes (ideal conductor or good conductor). In that section, we retrieve the important result [16–18] that for charge asymmetric electrolytes, a nonzero potential difference builds up between each electrode and the middle of the electrolyte solution and the system is not locally neutral, although both confining plates are grounded.

II. MODEL

As explained in Sec. I the system under consideration is an electrolyte confined between two grounded conductor planar electrodes separated by a distance W. Let us choose the x axis in the direction perpendicular to the electrodes, the origin is in the middle of the electrodes and the electrodes are located at $x = \pm W/2$. We will eventually also consider the limiting case when $W \to \infty$. In this case, we shall use the coordinate $X = x + W/2$ which measures the distance from one electrode.

We will model the electrolyte as composed of several species of pointlike micro-ions with charges q_α labeled by a Greek index. The solvent will be modeled as a continuum medium with dielectric constant ε. As is well known [19,20], a system of charged point particles described by classical statistical mechanics is not stable. In principle, we should introduce some short-distance cutoff, for instance, the radius of the ions, to avoid the collapse of particles of different signs. However, in the low coupling regime considered here, most physical quantities have a well-defined value when this short-distance cutoff vanishes. Therefore, our model will give valuable quantitative information on the system provided the ion radius is much smaller that the others lengths involved in the problem.

The position of the ith particle of the species α will be labeled as $\mathbf{r}_{\alpha,i}$. We shall work in the grand-canonical ensemble at a reduced inverse temperature $\beta = 1/(k_B T)$, with k_B the Boltzmann constant and T the absolute temperature. The average number of particles $\langle N_\alpha \rangle$ of the species α is controlled by the chemical potential μ_α. We shall use the fugacity $\zeta_\alpha = e^{\beta \mu_\alpha}/\Lambda_\alpha^3$ where Λ_α is the thermal de Broglie wavelength of the particles, which appears as usual in classical (i.e., nonquantum) statistical mechanics after the trivial Gaussian integration over the kinetic part of the Hamiltonian. We shall impose the pseudoneutrality condition

$$\sum_\alpha q_\alpha \zeta_\alpha = 0. \qquad (2.1)$$

In Appendix B of Ref. [14], it is explained that this choice is equivalent to suppose that there is no electric potential difference between the plates and the interior of the system in the mean field approximation. The pseudoneutrality condition ensures the neutrality of the reservoir, however, as we will see below, it does not ensure the global neutrality of the system confined with Dirichlet boundary conditions. As we

will show in Sec. IV, there is a nonvanishing charge density near the electrodes. However, this charge density induces in the electrodes a polarization charge of opposite sign and the total charge (system plus electrodes) is zero.

There are two models that can be used to describe the electrodes [15,21]. The simpler one is the ideal conductor model. In this model, the interaction potential between two unit charges located at $\mathbf{r} = (x, y, z)$ and $\mathbf{r}' = (x', y', z')$ is the solution of Poisson equation

$$\Delta v(\mathbf{r}, \mathbf{r}') = -\frac{4\pi}{\varepsilon} \delta(\mathbf{r} - \mathbf{r}'), \qquad (2.2)$$

satisfying the Dirichlet boundary conditions $v(\mathbf{r}, \mathbf{r}') = 0$ if $x' = \pm W/2$. It can be computed using, for example, the method of images,

$$v(\mathbf{r}, \mathbf{r}') = \frac{1}{\varepsilon} \sum_{n=-\infty}^{+\infty} \left[\frac{1}{[(x - x' + 2nW)^2 + (\mathbf{r}_\perp - \mathbf{r}'_\perp)^2]^{1/2}} - \frac{1}{[(x + x' + (2n+1)W)^2 + (\mathbf{r}_\perp - \mathbf{r}'_\perp)^2]^{1/2}} \right], \qquad (2.3)$$

where $\mathbf{r}_\perp = (y, z)$ is the transversal part of the position vector $\mathbf{r}$ and ε is the dielectric constant of the solvent. For future reference, we define the Coulomb potential for an unconfined system as

$$v^0(\mathbf{r}, \mathbf{r}') = \frac{1}{\varepsilon} \frac{1}{|\mathbf{r} - \mathbf{r}'|}, \qquad (2.4)$$

which will be needed in the following.

Notice that with this ideal conductor model, the microscopic electric potential deduced from (2.3) vanishes on the electrodes, for any configuration of the system. Then, not only the average electric potential will vanish on the electrodes, but also its fluctuations.

In a real situation, even if the electrodes have very good conducting properties, the electric potential inside the conductor will be subjected to thermal fluctuations. This leads us to the other model that can be used to describe the electrodes, the good conductor model. In this model, the electrodes are genuine Coulomb systems with good conducting properties. We will restrict ourselves to a classical (nonquantum) description of these conductors. We will consider that the screening length in the conductors vanishes. This ensures that the electrodes have good conducting properties. It is shown in [15] that in this limit the average electric potential vanishes on the electrodes. However, the fluctuations of the potential do not vanish in this limit.

A natural question then arises: how are related the ideal conductor model and the good conductor one? This question has already been addressed in Ref. [15] and we will make extensive use of the results presented there. It is shown in Ref. [15] that the densities and electric potential profiles inside the electrolyte are the same in both models. Thus, we will work with the (more simpler) ideal conductor model for the determination of these profiles in Sec. IV.

On the other hand, the results for the grand potential and for the pressure are different in both models, but there are simple relations between them [15]. We will use the ideal conductor model for the calculation of these quantities in Sec. III and using the relations found in [15], we will obtain the results for good conductor model. From now on, we consider the ideal conductor model unless stated otherwise.

Although to write down the Hamiltonian of the system is a trivial exercise in electrostatics, to clearly show what the problem is with the previous study [13] of this system, we will detail a few (well-known) points before proceeding. First, consider the case when only a planar electrode is located at $X=0$. Bringing first a unit charge from infinity to a position $\mathbf{r}=(X,y,z)$ at a distance X from the plane cost a nonzero energy, contrary to the case of an unconfined system. This is because of the interaction between the particle and the polarization charge it induces in the plane. In this very simple geometry, this interaction can also be understood as the potential energy between the particle and an image charge located at $\mathbf{r}^*=(-X,y,z)$. This energy is $-1/(4\varepsilon X)$, which can be formally written as $(1/2)[v(\mathbf{r},\mathbf{r})-v^0(\mathbf{r},\mathbf{r})]$ [in this case $v(\mathbf{r},\mathbf{r}')$ is the potential $(|\mathbf{r}-\mathbf{r}'|^{-1}-|\mathbf{r}-\mathbf{r}^*|^{-1})/\varepsilon$ when only one electrode is present]. This interaction energy should be included in the Hamiltonian.

Following the same lines, in the general case of two metallic planes, the potential energy of the system reads

$$H = \frac{1}{2}\sum_{\alpha,\gamma}\sum_{i,j}{}' q_\alpha q_\gamma v(r_{\alpha,i},\mathbf{r}_{\gamma,j}) + \frac{1}{2}\sum_\alpha\sum_i q_\alpha^2 [v(\mathbf{r}_{\alpha,i},\mathbf{r}_{\alpha,i})$$
$$-v^0(\mathbf{r}_{\alpha,i},\mathbf{r}_{\alpha,i})]. \qquad (2.5)$$

In the first sum, the prime means that the case $\alpha=\gamma$ and $i=j$ should be omitted. The second sum is the energy between each particle and the polarization charge it has induced in the electrodes, as discussed previously. Introducing the microscopic charge density defined as

$$\hat{\rho}(\mathbf{r}) = \sum_\alpha\sum_i q_\alpha\delta(\mathbf{r}-\mathbf{r}_{\alpha,i}), \qquad (2.6)$$

we can formally write the potential part of the Hamiltonian of the system as

$$H = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\hat{\rho}(\mathbf{r})v(\mathbf{r},\mathbf{r}')\hat{\rho}(\mathbf{r}') - \frac{1}{2}\sum_\alpha\sum_{i-1}^{N_\alpha}q_\alpha^2 v^0(\mathbf{r}_{\alpha,i},\mathbf{r}_{\alpha,i}). \qquad (2.7)$$

The domain of integration in the first term is the space between the two parallel electrodes ($-W/2<x<W/2$). Notice that from the first term written in terms of "continuous" fields we subtract the infinite "self-energy" of a particle $v^0(\mathbf{r},\mathbf{r})$, but with the potential energy v^0 corresponding to an unconfined system.

With the Coulomb potential v^0 given by Eq. (2.4) this self-energy is infinite. The appearance of infinite quantities can be avoided, and the subsequent analysis can be done more rigorously by modifying the Coulomb potential $v^0(\mathbf{r},\mathbf{r}')$ by introducing a short-distance cutoff that smears out the singularity at $\mathbf{r}=\mathbf{r}'$. At the end of the calculations,

one can then take the limit of a vanishing cutoff. This has been done rigorously in Ref. [22]. It turns out that the final results are the same as if one takes the short-distance cutoff equal to zero from the start. Therefore, to simplify the algebra we will take from the start a system of point particles without short-distance cutoff.

Now we follow the method proposed recently by the author and collaborators in Refs. [14,23] to study in general confined Coulombic systems in a low coupling regime. Let us define the Coulombic couplings $\Gamma_\alpha=\beta q_\alpha^2\zeta_\alpha^{1/3}/\varepsilon$. The method proposed in Ref. [14] is valid for $\Gamma_\alpha\ll 1$.

In the method exposed in Ref. [14], the sine-Gordon transformation [24] is performed in the grand-canonical partition function, and the action of the corresponding field theory is then expanded to the quadratic order (valid in the low Coulombic coupling regime) around the stationary (mean-field) solution (here $\phi=0$). For details, the reader is referred to Ref. [14] and to Appendix A. The grand partition function can then be written as

$$\Xi = \frac{1}{Z_G}\int \mathcal{D}\phi \exp[-S(\phi)], \qquad (2.8)$$

with

$$Z_G = \int \mathcal{D}\phi \exp\left\{ -\frac{1}{2}\int \phi(\mathbf{r})\left[-\frac{\beta\varepsilon\Delta}{4\pi}\right]\phi(\mathbf{r})d\mathbf{r}\right\}, \qquad (2.9)$$

and $S(\phi)$ is an action, quadratic in ϕ, given by

$$S(\phi) = \frac{1}{2}\int \frac{-\beta\varepsilon}{4\pi}\phi(\mathbf{r})\Delta\phi(\mathbf{r}) + \sum_\gamma (\beta q_\gamma)^2\zeta_\gamma :: \phi(\mathbf{r})^2 :: d\mathbf{r}, \qquad (2.10)$$

where $:: \phi(\mathbf{r})^2 ::$ is a pseudonormal ordered product, (see Appendix A for details).

The field $\phi(\mathbf{r})$ is a mathematical intermediary. At the mean-field level, the stationary equation for the action (before it is expanded to the quadratic order) is Poisson–Boltzmann equation, and $i\phi(\mathbf{r})$ can be interpreted as the electric potential. However, this relation breaks down when we consider the fluctuations as in the present case, for instance, the correlations of $\phi(\mathbf{r})$ are short-ranged [25], whereas the correlations of the electric potential are known to be long-ranged [26,27]. The Gaussian functional integration in Eq. (2.8) can be performed [14] to obtain

$$\Xi = \left[\prod_n \left(1-\frac{\kappa^2}{\lambda_n}\right)\prod_m e^{\frac{\kappa^2}{\lambda_m^0}}\right]^{-1/2} e^{\sum_\alpha V\zeta_\alpha}, \qquad (2.11)$$

where λ_n are the eigenvalues of the Laplacian operator satisfying the Dirichlet boundary conditions and λ_m^0 are the eigenvalues of the Laplacian operator defined in the whole space $\mathbb{R}^3$ without boundaries. We will call this case, in the following, the free boundary conditions case. The volume of the system is V and $\kappa=\sqrt{\sum_\alpha 4\pi\zeta_\alpha\beta q_\alpha^2/\varepsilon}$ is the inverse Debye length. The second product in Eq. (2.11) involving λ_m^0 comes from the subtraction of the self-energy term $v^0(\mathbf{r},\mathbf{r})$.

III. GRAND POTENTIAL AND PRESSURE

A. Ideal conductor model

In this part, we use the ideal conductor model to describe the electrode. In what follows, we will use a superscript "id" in the thermodynamic quantities.

1. Grand potential

For the present geometry, the eigenvalues of the Laplacian for Dirichlet boundary conditions and free boundary conditions, respectively, are $\lambda = -\mathbf{k}^2 - (n\pi)^2/W^2$ with $n \in \mathbb{N}^*$ and $\mathbf{k} \in \mathbb{R}^2$ and $\lambda_m^0 = -\mathbf{K}^2$ with $\mathbf{K} \in \mathbb{R}^3$. We find that the grand potential Ω^{id} takes the form $\Omega^{\text{id}} = \Omega_{\text{ig}} + \Omega_{\text{exc}}^{\text{id}}$, with $\Omega_{\text{ig}} = k_B T V \Sigma_\alpha \zeta_\alpha$ the ideal gas contribution and $\Omega_{\text{exc}}^{\text{id}}$ the excess grand potential. From Eq. (2.11), we find the excess grand potential $\omega_{\text{exc}}^{\text{id}}$ per unit area of a plate, as

$$\beta\omega_{\text{exc}}^{\text{id}} = \frac{1}{2(2\pi)^2}\int_{\mathbb{R}^2} \ln\prod_{n=1}^{\infty}\left(1 + \frac{\kappa^2}{\left(\frac{n\pi}{W}\right)^2 + \mathbf{k}^2}\right)d^2\mathbf{k}$$
$$- \frac{W\kappa^2}{2(2\pi)^3}\int_{\mathbb{R}^3}\frac{d^3\mathbf{K}}{\mathbf{K}^2}. \qquad (3.1)$$

The product under the logarithm can be performed exactly [28] to obtain

$$\beta\omega_{\text{exc}}^{\text{id}} = \frac{1}{4\pi}\int_0^{k_{\max}} \ln\left[\frac{k}{\sqrt{\kappa^2 + k^2}}\frac{\sinh(W\sqrt{\kappa^2 + k^2})}{\sinh(kW)}\right]k\,dk$$
$$- \frac{W\kappa^2}{(2\pi)^2}\int_0^{K_{\max}}dK. \qquad (3.2)$$

Notice that we introduced two ultraviolet cutoffs $k_{\max}$ and $K_{\max}$ for both integrals since each integral, taken separately, is ultraviolet divergent. However, together they should give a finite result when $k_{\max} \to \infty$ and $K_{\max} \to \infty$ *as far as the bulk properties are concerned*. Indeed, in the limit $W \to \infty$ we should recover the well-known bulk result [14,22] $\beta\omega_b = -\kappa^3 W/(12\pi)$. This requirement imposes that the cutoffs should be related by $K_{\max} = \pi k_{\max}/2$. Doing the change of variable $K = \pi k/2$ in the second integral, the excess grand potential per unit area can finally be written as

$$\beta\omega_{\text{exc}}^{\text{id}} = \frac{1}{4\pi}\int_0^{k_{\max}}\left[k\ln\left(\frac{k}{\sqrt{\kappa^2 + k^2}}\frac{\sinh(W\sqrt{\kappa^2 + k^2})}{\sinh(kW)}\right)\right.$$
$$\left. - \frac{\kappa^2 W}{2}\right]dk. \qquad (3.3)$$

In principle, we should take the limit $k_{\max} \to \infty$, however, it should be noted that the above expression has a logarithmic divergence when $k_{\max} \to \infty$, which manifests itself in the surface tension. This can be seen clearly if we expand ω_{exc} for $\kappa W \gg 1$, as

$$\beta\omega_{\text{exc}}^{\text{id}} = -\frac{\kappa^3 W}{12\pi} + 2\beta\gamma + \frac{\zeta(3)}{16\pi W^2} + \mathcal{O}(e^{-2\kappa W}), \quad (3.4)$$

with the surface tension γ given by

$$\beta\gamma = \frac{\kappa^2}{16\pi}\left(\ln\frac{\kappa}{k_{\max}} - \frac{1}{2}\right) \qquad (3.5)$$

and $\zeta(3)$ is the Riemann zeta function evaluated at 3 (not to be confused with the fugacities). In Eq. (3.4), all terms that vanish when $k_{\max} \to \infty$ have been omitted.

A few comments are in order. Concerning the surface tension γ, it is divergent when the cutoff $k_{\max} \to \infty$. This is normal: it is due to the strong attraction that each particle and its images of opposite charge in the electrodes feel. The small coupling regime of an electrolyte near a plane metallic wall can also by studied from a diagrammatic Mayer expansion. This is done in section 5 of Ref. [29] for a two-dimensional Coulombic system. These calculations can easily be adapted to a three-dimensional system to show that the surface tension γ is related to the integral of the screened interaction energy between a particle and its image: $-\exp(-2\kappa X)/(4X)$. This energy is not integrable at short distances and its integral has a logarithmic divergence at $X=0$. In this picture, one can impose a short-distance cutoff D: the particles cannot approach below this distance to the electrode, and the surface tension is proportional to $\ln \kappa D$. Actually, our ultraviolet cutoff $k_{\max} \propto 1/D$.

The second comment concerns the algebraic finite-size correction $k_B T\zeta(3)/(16\pi W^2)$ to the grand potential. This finite-size correction is universal, it does not depend on the details of the microscopic constitution of the system, and it has been proved to exist even beyond the low coupling regime considered here provided that the electrolyte is in a conducting phase and it has good screening properties, in particular if it can screen an external infinitesimal dipole [30]. This correction is a consequence only of the screening properties of the system: that explains its universality. However, as we will see later, this term is only present for the ideal conductor model considered in this section. For the good conductor model, this algebraic correction in the grand potential is absent.

We should also mention that this algebraic finite-size correction is not present in the case of insulating plates [30–32]. Indeed, if the boundary is made of a dielectric material, there is a subtle cancellation between the term found here and the one from the Lifshitz interaction (the Casimir effect). For dielectric boundary conditions, the disjoining pressure has an exponential decay $e^{-2\kappa W}$ at large separations W and it is attractive [31,32], as opposed to the present case of ideal conductor boundary conditions. Further details on this interesting difference are discussed in Appendix B.

2. Pressure

The pressure is obtained from the usual relation $p = -\partial\omega/\partial W$. From Eq. (3.3), we find that the excess pressure $p_{\text{exc}}^{\text{id}}$ is given by

$$\beta p_{\text{exc}}^{\text{id}} = \frac{1}{4\pi}\int_0^\infty\left[\frac{\kappa^2}{2} + k^2\coth(kW)\right.$$
$$\left. - k\sqrt{k^2 + \kappa^2}\coth(W\sqrt{k^2 + \kappa^2})\right]dk. \qquad (3.6)$$

Although the grand potential has an ultraviolet divergence

and should be regularized as explained earlier, the pressure proves to be well defined for $k_{max} \to \infty$ (and $W \neq 0$). This is expected since from the large-W expansion (3.4) of the grand potential, we can see that the ultraviolet divergent part (the surface tension contribution) does not depend on W. Notice, however, that for $W \to 0$ the pressure is divergent. Let us mention that the nondivergence of the pressure with the cutoff and, more precisely, the fact that it is independent of the surface tension γ is special to this planar geometry. If we were to consider a confining geometry with curved boundaries (for example an electrolyte confined in a spherical domain), the surface tension would be a dominant term in the pressure: due to the curvature R the disjoining pressure for large systems would be $p_d \propto -\gamma/R$, see Ref. [33] for an example of this effect.

Doing a few manipulations to Eq. (3.6), we can cast the pressure in a form more adequate to study the disjoining pressure p_d^{id}, difference between the pressure p^{id} and the bulk pressure p^b, and its large-W behavior. The bulk pressure, expressed in terms of the fugacities, is obtained from the limit $W \to \infty$ of Eq. (3.4), and it is given by

$$\beta p^b = \sum_\alpha \zeta_\alpha + \frac{\kappa^3}{12\pi}. \tag{3.7}$$

The well-known expression of the bulk pressure in terms of the densities will be recovered in the Eq. (4.17), when we obtain the expression of the bulk densities in terms of the fugacities.

We then find the disjoining pressure

$$\beta p_d^{id} = \frac{\zeta(3)}{8\pi W^3} + \frac{\kappa^3}{4\pi} \int_0^\infty u\sqrt{u^2+1}\left[1 - \coth(\kappa W\sqrt{u^2+1})\right]du \tag{3.8}$$

$$\underset{W \to \infty}{=} \frac{\zeta(3)}{8\pi W^3} + \mathcal{O}(e^{-2\kappa W}). \tag{3.9}$$

For large separations W of the electrode plates, the disjoining pressure is positive and decays as $1/W^3$. The force exerted on the plates is therefore repulsive and the system is stable: if it is compressed the pressure increases. This actually holds for any separation, as can be seen in Fig. 1.

B. Good conductor model

We now study the electrolyte confined by good conductor electrodes. We will not use any superscript in the thermodynamic quantities in order to differentiate them from the ones computed for the ideal conductor model.

1. Free energy and grand potential

Let F be the free energy of the system composed of the electrolyte and the electrodes. These latter ones are considered as Coulomb systems with a vanishing screening length (high density of charged particles) in the region $x < -W/2$ and $x > W/2$. The electrolyte is in the region $-W/2 < x < W/2$.
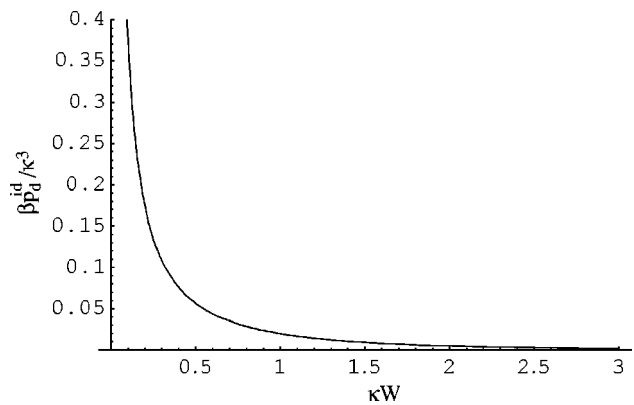

FIG. 1. The disjoining pressure of the electrolyte confined by ideal conductor electrodes. It is positive and always decreasing with increasing W, indicating that there is a repulsive force between the two ideal conductor parallel plates.

For the following discussion, it is useful to introduce F_0 the free energy of the electrodes in absence of the electrolyte. It is shown in Ref. [15] that $F = F^{id} + F_0$, where F^{id} is the free energy of the electrolyte in the ideal conductor model, which can be obtained from the results of the previous section. The argument of Ref. [15] can easily be applied to the grand potential, thus,

$$\omega = \omega^{id} + \omega_0, \tag{3.10}$$

with ω the grand potential (per unit area of the plates) of the system when the electrodes are described as good conductors, ω^{id} the grand potential (per unit area) for the ideal conductor model, which can be obtained from Eq. (3.3), and ω_0 the grand potential of the good conducting electrodes alone in the space in the absence of the electrolyte.

The large-W expansion of this latter term ω_0 is given by Lifshitz theory [34] in the classical regime as $-k_B T\zeta(3)/(16\pi W^2)$. Thus, it cancels the similar contribution that we found in ω^{id} in Eq. (3.4). When the electrodes are described as good conductors (which is a more realistic model), there is no long-range contribution in $1/W^2$ to the grand potential of the system, as opposed to the ideal conductor model.

2. Pressure

The pressure is the force per unit area that the electrolyte exerts on one plate, say the one at $x = W/2$. It can be computed by means of the Maxwell stress tensor $T_{\mu\nu}$. It is $p = -T_{xx}$ evaluated at $x = W/2$. In Ref. [15], it is shown that the stress tensor in the ideal conductor model $T_{\mu\nu}^{id}$ and the one in the good conductor model $T_{\mu\nu}$ are related by

$$T_{\mu\nu}(\mathbf{r}) - T_{\mu\nu}^{id}(\mathbf{r}) = \frac{\varepsilon}{4\pi}\left(\partial_\mu\partial_\nu' - \frac{\delta_{\mu\nu}}{2}\partial_\sigma\partial_\sigma'\right)G^*(\mathbf{r},\mathbf{r}')_{\mathbf{r}'=\mathbf{r}}, \tag{3.11}$$

with $G^*(\mathbf{r},\mathbf{r}') = v^0(\mathbf{r},\mathbf{r}') - v(\mathbf{r},\mathbf{r}')$ is (minus) the "images" contribution to the Coulomb potential v in the ideal conductor model.
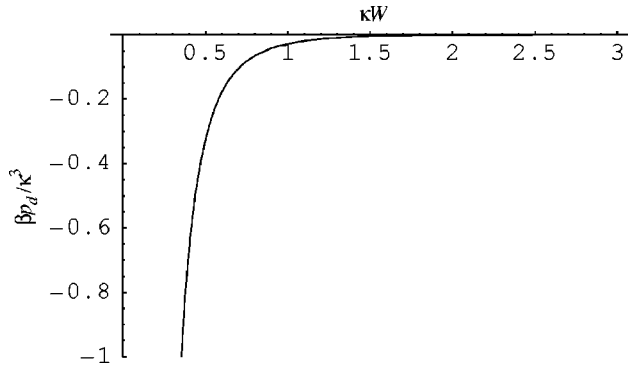
FIG. 2. The disjoining pressure of the electrolyte confined by good conductor electrodes. It is negative and always increasing with increasing W, indicating that there is an attractive force between the two conductor parallel plates.

The right-hand side of Eq. (3.11) can be computed explicitly, giving

$$T_{xx} - T_{xx}^{\text{id}} = \frac{\zeta(3)}{8\pi W^3}. \tag{3.12}$$

Thus, the pressure for the good conductor model is

$$p = p^{\text{id}} - \frac{\zeta(3)}{8\pi W^3}. \tag{3.13}$$

Using Eq. (3.8), we finally obtain the disjoining pressure when the electrodes are modeled as good conductors:

$$\beta p_d = \frac{\kappa^3}{4\pi} \int_0^\infty u\sqrt{u^2+1}[1 - \coth(\kappa W\sqrt{u^2+1})]du. \tag{3.14}$$

Notice that since the function coth in the integrand is greater than 1, the disjoining pressure is always negative. Figure 2 shown a plot of the disjoining pressure as a function of the width W. We notice that the pressure is now an increasing function of W. This behavior is just the opposite of that obtained with the ideal conductor model. Now, for large W as well, the disjoining pressure decays exponentially as $e^{-2\kappa W}$.

IV. DENSITY AND ELECTRIC POTENTIAL PROFILES

The difference in the results for the pressure using the ideal conductor model and the good conductor one are drastic. However, the results for the density and electric potential profiles inside the electrolyte are the same in both models, as was shown in Ref. [15]. Therefore, we will concentrate in this section on the ideal conductor model, which is more tractable.

A. Density

The density $n_\alpha(\mathbf{r})$ can be obtained from the usual functional derivative.

$$n_\alpha(\mathbf{r}) = \zeta_\alpha(\mathbf{r})\frac{\delta \ln \Xi}{\delta \zeta_\alpha(\mathbf{r})}. \tag{4.1}$$

In Appendix A, it is shown that

$$n_\alpha(\mathbf{r}) = \zeta_\alpha\bigg(1 - \frac{\beta q_\alpha^2}{2}[v_{\text{DH}}(\mathbf{r},\mathbf{r}) - v^0(\mathbf{r},\mathbf{r})]$$
$$+ \frac{\beta^2 q_\alpha}{2}\sum_\gamma \zeta_\gamma q_\gamma^3 \int v_{\text{DH}}(\mathbf{r}',\mathbf{r})[v_{\text{DH}}(\mathbf{r}',\mathbf{r}')$$
$$- v^0(\mathbf{r}',\mathbf{r}')]d\mathbf{r}'\bigg), \tag{4.2}$$

where $v_{\text{DH}}(\mathbf{r},\mathbf{r}')$ is the Debye-Hückel (DH) potential, solution of DH equation

$$(\Delta - \kappa^2)v_{\text{DH}}(\mathbf{r},\mathbf{r}') = -\frac{4\pi}{\varepsilon}\delta(\mathbf{r}-\mathbf{r}'), \tag{4.3}$$

satisfying the Dirichlet boundary conditions $v_{\text{DH}}(\mathbf{r},\mathbf{r}')=0$ if $x' = \pm W/2$. Equation (4.2) gives the density up to the order $\Gamma_\alpha^{3/2}$ in the Coulombic couplings. For the present calculations, we found that the most convenient form for v_{DH} is as a Fourier transform in the transverse direction $\mathbf{r}_\perp = (y,z)$. In Fourier transform, DH Eq. (4.3) reduces to an ordinary linear differential equation in the x variable, which can be easily solved. We then find

$$v_{\text{DH}}(\mathbf{r},\mathbf{r}') = \frac{4\pi}{\varepsilon}\int_{\mathbb{R}^2}\frac{d\mathbf{k}}{(2\pi)^2}\frac{\sinh[\sqrt{k^2+\kappa^2}(W/2-x')]\sinh[\sqrt{k^2+\kappa^2}(W/2+x)]}{\sqrt{k^2+\kappa^2}\sinh(W\sqrt{k^2+\kappa^2})}e^{i\mathbf{k}\cdot\mathbf{r}_\perp}, \tag{4.4}$$

if $x<x'$ and exchange the roles of x and x' if $x'<x$. Using this expression in (4.4), we find that the density can be expressed as

$$n_\alpha(x) = \zeta_\alpha\left[1 + \frac{\beta q_\alpha^2 \kappa}{2\epsilon}f_1(\kappa x) + \frac{2\pi\beta^2 q_\alpha \sum_\gamma q_\gamma^3 \zeta_\gamma}{\kappa\varepsilon^2}f_2(\kappa x)\right], \tag{4.5}$$

with

$$f_1(\tilde{x}) = -\int_0^\infty \left\{ \frac{2k}{\sqrt{k^2+1}} \frac{\sinh[\sqrt{k^2+1}(\tilde{W}/2-\tilde{x})]\sinh[\sqrt{k^2+1}(\tilde{W}/2+\tilde{x})]}{\sinh(\sqrt{k^2+1}\tilde{W})} - 1 \right\} dk \tag{4.6}$$

and

$$f_2(\tilde{x}) = \frac{\cosh\tilde{x}}{\cosh(\tilde{W}/2)} \int_0^\infty \left[1 - \frac{4k\sqrt{k^2+1}}{4k^2+3}\coth(\tilde{W}\sqrt{k^2+1}) \right] dk \tag{4.7}$$

$$+ \int_0^\infty \frac{k\cosh(2\tilde{x}\sqrt{k^2+1})}{\sqrt{k^2+1}(4k^2+3)\sinh(\tilde{W}\sqrt{k^2+1})} dk \tag{4.8}$$

$$+ \int_0^\infty \left[\frac{k}{\sqrt{k^2+1}}\coth(\tilde{W}\sqrt{k^2+1}) - 1 \right] dk, \tag{4.9}$$

where we have used distances measured in Debye length units $\tilde{x}=\kappa x$ and $\tilde{W}=\kappa W$. Notice that the factors multiplying f_1 and f_2 in the density, Eq. (4.5), are of order $\Gamma_\alpha^{3/2}$ in the coulombic couplings. Our approach neglects corrections of higher order than $\Gamma_\alpha^{3/2}$.

After doing the change of variable $u=\sqrt{k^2+1}$ in the above integrals, some of them can be performed explicitly, and doing some manipulations, we find the following convenient expressions for $f_1(\tilde{x})$ and $f_2(\tilde{x})$:

$$f_1(\tilde{x}) = 1 + \frac{e^{-(\tilde{W}-2\tilde{x})}}{\tilde{W}-2\tilde{x}} + \frac{e^{-(\tilde{W}+2\tilde{x})}}{\tilde{W}+2\tilde{x}} + 2\int_1^\infty \frac{e^{-3u\tilde{W}}\cosh(2u\tilde{x})du}{1-e^{-2u\tilde{W}}}$$

$$+ \frac{1}{\tilde{W}}\ln(1-e^{-2\tilde{W}}) \tag{4.10}$$

and

$$f_2(\tilde{x}) = f_2^{(1)}(\tilde{x}) + f_2^{(2)}(\tilde{x}) - 1 - \frac{1}{\tilde{W}}\ln(1-e^{-2\tilde{W}}), \tag{4.11}$$

with

$$f_2^{(1)} = \frac{\cosh\tilde{x}}{\cosh(\tilde{W}/2)} \left[1 - \frac{\ln 3}{4} - 8\int_1^\infty \frac{u^2 e^{-2u\tilde{W}}}{(4u^2-1)(1-e^{-2u\tilde{W}})} du \right] \tag{4.12}$$

and

$$f_2^{(2)}(\tilde{x}) = \frac{1}{4}\left\{ e^{\tilde{W}/2-\tilde{x}}\mathrm{Ei}\left[-3\left(\frac{\tilde{W}}{2}-\tilde{x}\right) \right] \right.$$

$$\left. - e^{-(\tilde{W}/2-\tilde{x})}\mathrm{Ei}\left[-\left(\frac{\tilde{W}}{2}-\tilde{x}\right) \right] \right\}, \tag{4.13a}$$

$$+ \frac{1}{4}\left\{ e^{\tilde{W}/2+\tilde{x}}\mathrm{Ei}\left[-3\left(\frac{\tilde{W}}{2}+\tilde{x}\right) \right] - e^{-(\tilde{W}/2-\tilde{x})}\mathrm{Ei}\left[-\left(\frac{\tilde{W}}{2}+\tilde{x}\right) \right] \right\}, \tag{4.13b}$$

$$+ 2\int_1^\infty \frac{e^{-3u\tilde{W}}\cosh(2u\tilde{x})du}{(4u^2-1)(1-e^{-2u\tilde{W}})}, \tag{4.13c}$$

where $\mathrm{Ei}(z)=-\int_{-z}^\infty e^{-t}/t\,dt$ is the exponential integral function. The advantage of these latter expressions is that one can immediately see that the terms written as integrals are of order $\mathcal{O}(e^{-2\tilde{W}})$ when $\tilde{W}\to\infty$. Therefore, we can easily obtain the expression for density in the case of one electrode alone, with $X=x+W/2$, as

$$n_\alpha(X) = \zeta_\alpha \left\{ 1 + \frac{\beta q_\alpha^2 \kappa}{2\varepsilon}\left(1 + \frac{e^{-2\kappa X}}{2\kappa X} \right) \right.$$

$$+ \frac{2\pi\beta^2 q_\alpha \sum_\gamma q_\gamma^3 \zeta_\gamma}{\varepsilon^2 \kappa}\left[e^{-\kappa X}\left(1 - \frac{\ln 3}{4} \right) \right.$$

$$\left. \left. + \frac{e^{\kappa X}\mathrm{Ei}(-3\kappa X) - e^{-\kappa X}\mathrm{Ei}(-\kappa X)}{4} - 1 \right] \right\}. \tag{4.14}$$

Far away from the metallic wall, $X\to\infty$, we find the bulk density

$$n_\alpha^b = \zeta_\alpha\left(1 + \frac{\beta q_\alpha^2 \kappa}{2\varepsilon} - \frac{2\pi\beta^2 q_\alpha \sum_\gamma q_\gamma^3 \zeta_\gamma}{\varepsilon^2 \kappa} \right). \tag{4.15}$$

Replacing back into Eq. (4.14), we find an expression for the density profile in terms of the bulk density

$$n_\alpha(X) = n_\alpha^b\left\{ 1 + \frac{\beta q_\alpha^2 e^{-2\kappa_{\mathrm{DH}}X}}{4\varepsilon X} \right. \tag{4.16a}$$

$$+ \frac{2\pi\beta^2 q_\alpha \sum_\gamma q_\gamma^3 n_\gamma^b}{\varepsilon^2 \kappa_{\mathrm{DH}}}\left[e^{-\kappa_{\mathrm{DH}}X}\left(1 - \frac{\ln 3}{4} \right) \right.$$

$$\left. \left. + \frac{e^{\kappa_{\mathrm{DH}}X}\mathrm{Ei}(-3\kappa_{\mathrm{DH}}X) - e^{-\kappa_{\mathrm{DH}}X}\mathrm{Ei}(-\kappa_{\mathrm{DH}}X)}{4} \right] \right\}. \tag{4.16b}$$

with corrections of higher order than $\Gamma_\alpha^{3/2}$. Here, $\kappa_{\mathrm{DH}} = \sqrt{4\pi\beta\sum_\gamma n_\gamma^b q_\gamma^2/\varepsilon}$. We recover the expression that Aqua and Cornu have previously obtained in their studies of the properties of a classical Coulombic system near a wall [16–18]

using diagrammatic methods, up to a small difference: the first term (4.16a) appears in [18] as an exponential Boltzmann factor of the screened interaction between a particle and its image. Here, this exponential Boltzmann factors appears linearized since the Coulombic coupling is small. Our density profile and the one found in [18] will agree, in the low coupling regime considered here, for distances not to close to the electrode and our results are reliable in this case. On the other hand, very close to the electrode, at distances comparable to the ion radius, our results will differ from those of Ref. [18], this is a defect of the pointlike model for the micro-ions used here.

We can use Eq. (4.15), which relates the fugacities to the bulk densities into the expression (3.7) of the bulk pressure expressed in terms of the fugacities, to recover the well-known equation of state of DH theory [4]:

$$\beta p^b = \sum_\alpha n_\alpha^b - \frac{\kappa_{DH}^3}{24\pi}. \tag{4.17}$$

Returning to the general case, for any arbitrary separation W of the plates, it can be noticed that the density diverges at $x=\pm W/2$ as $1/(x\mp W/2)$. The density does not have a finite value at the contact of the electrodes, but it diverges. This is an expected behavior, since each particle is strongly attracted to its images in the electrodes. This is related to the divergence of the surface tension and the necessity to impose a short-distance minimum distance of approach of the particles to the planar electrodes $D \propto 1/k_{max}$ as explained in the previous section. The logarithmic divergence in $\ln \kappa D$ of the surface tension is closely related to the divergence of the densities as $1/(x\mp W/2)$ at the contact of each electrode.

The charge density turns out to be

$$\rho(x) = \sum_\alpha q_\alpha n_\alpha(x) = \frac{\beta\kappa}{2\varepsilon}\left(\sum_\alpha \zeta_\alpha q_\alpha^3\right)\widetilde{\rho}(\kappa x), \tag{4.18}$$

with the reduced charge density

$$\widetilde{\rho}(\tilde{x}) = f_1(\tilde{x}) + f_2(\tilde{x}) \tag{4.19a}$$

$$= \frac{e^{-(\widetilde{W}-2\tilde{x})}}{\widetilde{W}-2\tilde{x}} + \frac{e^{-(\widetilde{W}+2\tilde{x})}}{\widetilde{W}+2\tilde{x}} + \frac{1}{4}\left\{e^{\widetilde{W}/2-\tilde{x}}\text{Ei}\left[-3\left(\frac{\widetilde{W}}{2}-\tilde{x}\right)\right]\right.$$

$$\left. - e^{-(\widetilde{W}/2-\tilde{x})}\text{Ei}\left[-\left(\frac{\widetilde{W}}{2}-\tilde{x}\right)\right]\right\} + \frac{1}{4}\left\{e^{\widetilde{W}/2+\tilde{x}}\text{Ei}\left[-3\left(\frac{\widetilde{W}}{2}+\tilde{x}\right)\right]\right.$$

$$\left. - e^{-(\widetilde{W}/2+\tilde{x})}\text{Ei}\left[-\left(\frac{\widetilde{W}}{2}+\tilde{x}\right)\right]\right\} + \left[1 - \frac{\ln 3}{4}\right.$$

$$\left. - 8\int_1^\infty \frac{u^2 e^{-2u\widetilde{W}}du}{(4u^2-1)(1-e^{-2u\widetilde{W}})}\right]\frac{\cosh\tilde{x}}{\cosh(\widetilde{W}/2)}$$

$$+ 8\int_1^\infty \frac{u^2 e^{-3u\widetilde{W}}\cosh(2u\tilde{x})du}{(4u^2-1)(1-e^{-2u\widetilde{W}})}. \tag{4.19b}$$

In the case of a two-component symmetric electrolyte, $q_1 = -q_2$, we have $\sum_\gamma \zeta_\gamma q_\gamma^3 = 0$, therefore, the system is locally neutral $\rho(x)=0$. For a general asymmetric electrolyte,
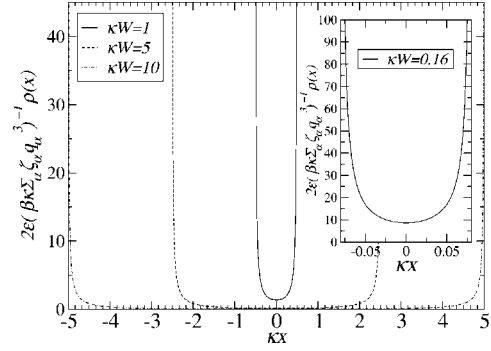

FIG. 3. The charge density profile in the slab for several values of the width W at fixed κ.

$\sum_\alpha q_\alpha^3 \zeta_\alpha \neq 0$ and the system is not locally neutral. Furthermore, the charge density diverges near the plates as $1/(x\mp W/2)$ which is not integrable. The total charge induced in the electrodes is infinite if the particles are allowed to approach the electrodes as near as they can.

Figure 3 shows several charge density profiles for different values of W with κ fixed. As expected, if $\kappa W \gg 1$, the profiles for different values of W are very similar since the corrections to the case $W \to \infty$ are of order $e^{-2\kappa W}$. This can be seen in the plots for $\kappa W=5$ and $\kappa W=10$ in Fig. 3. The differences from the case $W \to \infty$ can be only be noticed for small values of κW, as in the cases $\kappa W=1$ and $\kappa W=0.16$ of Fig. 3. However, let us remark that for any value of W, the charge density from an electrode up to the middle of the slab is strictly monotonic (increasing or decreasing depending on the sign of $\sum_\alpha \zeta_\alpha q_\alpha^3$).

B. Electric potential

For the present geometry, the electric potential can be computed from the charge density as

$$\Phi(x) - \Phi(0) = \frac{4\pi}{\varepsilon}\int_0^x (x'-x)\rho(x')dx'. \tag{4.20}$$

This gives

$$\Phi(x) - \Phi(0) = \frac{2\pi\beta}{\varepsilon^2\kappa}\left(\sum_\gamma q_\gamma^3 \zeta_\gamma\right)[\widetilde{\Phi}(\kappa x) - \widetilde{\Phi}(0)], \tag{4.21}$$

with the reduced electric potential

$$\widetilde{\Phi}(\tilde{x}) - \widetilde{\Phi}(0) = \frac{1}{2}[e^{\widetilde{W}/2}\text{Ei}(-3\widetilde{W}/2) - e^{-\widetilde{W}/2}\text{Ei}(-\widetilde{W}/2)] \tag{4.22a}$$

$$+ \frac{1}{4}\left\{e^{-(\widetilde{W}/2+\tilde{x})}\text{Ei}\left[-\left(\frac{\widetilde{W}}{2}+\tilde{x}\right)\right] - e^{\widetilde{W}/2+\tilde{x}}\text{Ei}\left[-3\left(\frac{\widetilde{W}}{2}+\tilde{x}\right)\right]\right\} \tag{4.22b}$$
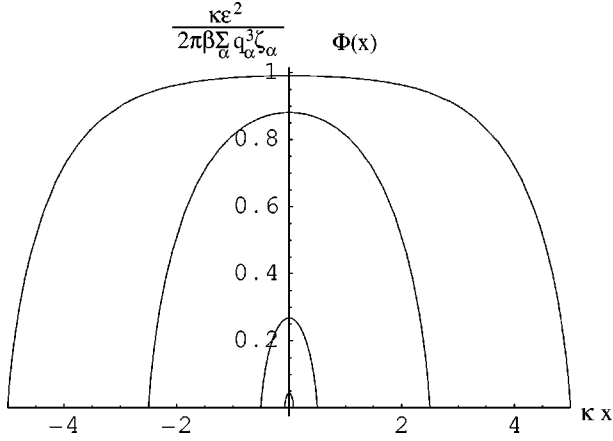
FIG. 4. The electric potential profile $\Phi(x)$ for different values of the width W of the slab at fixed κ. From top to bottom, $\kappa W = 10, 5, 1, 0.16$.

$$+\frac{1}{4}\left\{e^{-(\tilde{W}/2-\tilde{x})}\text{Ei}\left[-\left(\frac{\tilde{W}}{2}-\tilde{x}\right)\right]-e^{\tilde{W}/2-\tilde{x}}\text{Ei}\left[-3\left(\frac{\tilde{W}}{2}-\tilde{x}\right)\right]\right\}$$

(4.22c)

$$+\left[1-\frac{\ln 3}{4}-8\int_1^\infty\frac{u^2 e^{-2u\tilde{W}}du}{(4u^2-1)(1-e^{-2u\tilde{W}})}\right]\frac{1-\cosh\tilde{x}}{\cosh(\tilde{W}/2)}$$

(4.22d)

$$-2\int_1^\infty\frac{e^{-3u\tilde{W}}[\cosh(2u\tilde{x})-1]}{(4u^2-1)(1-e^{-2u\tilde{W}})}du.$$

(4.22e)

Figure 4 shows the electric potential profile for different values of the width W.

An interesting quantity is the potential difference between a plate (for example, $x=W/2$) and the middle of the slab ($x=0$), which can be obtained from the previous expression by replacing x by $W/2$ [the term (4.22c) in the previous equation has the limit $-(\ln 3)/4$ when $x=W/2$]. Figure 5 shows a plot of the potential difference between the middle of the slab and a plate $\Phi_0 = \Phi(0) - \Phi(\pm W/2) = \Phi(0)$ as a func-
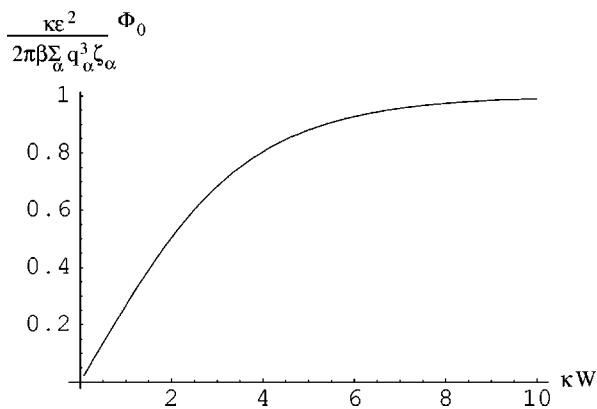

FIG. 5. The potential difference Φ_0 between the middle of the slab and one electrode as a function of the width W of the slab.

tion of W. It is interesting to know the limit when $W\rightarrow\infty$. From Eq. (4.22), we get

$$\Phi_0 \underset{W\rightarrow\infty}{=} \frac{2\pi\beta}{\varepsilon^2\kappa}\sum_\gamma q_\gamma^3\zeta_\gamma.$$

(4.23)

For an asymmetric electrolyte, a nonzero potential difference between the middle of the electrolyte and any plate builds up, although both plates are grounded. The sign of this potential difference is given by the parameter $\sum_\alpha\zeta_\alpha q_\alpha^3$. This potential difference is a monotonic function (increasing or decreasing depending on the sign of $\sum_\alpha q_\alpha^3\zeta_\alpha$) of the width W with an extremum value for $W\rightarrow\infty$ given by Eq. (4.23).

It is interesting to comment on a few points on the case when only one electrode is present, which has been previously studied by Aqua [18] using diagrammatic methods. In the limit $W\rightarrow\infty$, with $\tilde{X}=\tilde{x}+\tilde{W}/2$, from Eq. (4.22) we recover Aqua's expression for the electric potential:

$$\tilde{\Phi}(\tilde{X})-\tilde{\Phi}_0=\left(\frac{\ln 3}{4}-1\right)e^{-\tilde{X}}+\frac{1}{4}[e^{-\tilde{X}}\text{Ei}(-\tilde{X})-e^{\tilde{X}}\text{Ei}(-3\tilde{X})].$$

(4.24)

We can notice that far away from the electrode, the potential behaves as

$$\Phi(X)-\Phi_0\underset{X\rightarrow\infty}{\sim}\frac{2\pi\beta}{\varepsilon^2\kappa}\left(\sum_\gamma q_\gamma^3\zeta_\gamma\right)\left(\frac{\ln 3}{4}-1\right)e^{-\kappa X}=\Phi_{\text{eff}}\,e^{-\kappa X},$$

(4.25)

where we defined

$$\Phi_{\text{eff}}=\frac{2\pi\beta}{\varepsilon^2\kappa}\left(\sum_\gamma q_\gamma^3\zeta_\gamma\right)\left(\frac{\ln 3}{4}-1\right).$$

(4.26)

This result suggests the following interpretation. If we were to understand this result using a mean-field linearized Poisson-Boltzmann equation, we can suppose that the electrode has an effective potential Φ_{eff} given by Eq. (4.26). The potential of the electrode, which is zero in our case, gets additively renormalized by Φ_{eff} by the effect of the fluctuations around the mean field. This interpretation follows the same philosophy that the one of the theory of the renormalized charge in highly charged colloids [35,36], except that in this case the potential renormalization is due to the effect of the correlations and not to the nonlinear effects of the mean field theory. If the electrode was at a fixed potential V, the effective potential as seen far from the electrode would be $V+\Phi_{\text{eff}}$ [18].

In the spirit of this interpretation, notice that the renormalization of the potential Φ_{eff} is positive if $\sum_\alpha q_\alpha^3\zeta_\alpha$ is negative, and it is negative otherwise. This potential renormalization only occurs for asymmetric electrolytes.

It is interesting to mention that a similar situation occurs in the charge renormalization of colloids due to the nonlinear effects in the mean-field approach for asymmetric electrolytes, although in the other direction. Indeed if the charge (say, positive) of a colloid is high enough to be in a nonlinear regime, but small enough to be in a nonsaturation regime, it has been found that the first deviation (quadratic correction)

of the effective charge from the bare charge have the sign of $\Sigma_\alpha q_\alpha^3 \zeta_\alpha$ [37–39]. In particular, in an intermediate regime, the effective charge of the colloid could be higher than the bare charge if $\Sigma_\alpha q_\alpha^3 \zeta_\alpha$ has the same sign as the bare charge. This analogy is, however, only qualitative. The context in the case of colloids is somehow different from the one considered here. In the colloids the renormalization is due to the nonlinear effects of the mean-field approach, and here we considered the corrections due to the correlations.

V. SUMMARY AND CONCLUSION

We have obtained corrections due to fluctuations to the mean-field description of an electrolyte confined in a metallic slab of width W. We considered two models to describe the metallic electrodes. The ideal conductor model is more tractable, but it neglects the fluctuations of the potential inside the electrodes. For this (academic) model, the disjoining pressure of the system is always positive and it increases if the separation W decreases, indicating a repulsive force on the metallic plates by the electrolyte and a stable system. We also confirmed [30] that for large separations W, the disjoining pressure has an algebraic decay in W^{-3}, $p_d \sim [k_B T \zeta(3)/(8\pi)]W^{-3}$. This large-$W$ algebraic finite-size correction is universal: it does not depend on the microscopic constitution of the system.

For the more realistic model of the good conductor electrodes, the behavior of the pressure is completely different. There is no algebraic decay in $1/W^3$ in the pressure. Its decay is exponential $e^{-2\kappa W}$ at large distances. Furthermore the disjoining pressure is negative, thus suggesting that there is an attractive force between the electrodes.

We obtained some results for the density profiles and the electric potential which are independent of the model used to describe the electrodes. We retrieved [16–18] a very interesting behavior if the electrolyte is asymmetric, in particular if $\Sigma_\alpha q_\alpha^3 \zeta_\alpha \neq 0$. In this case the system is not locally neutral, there is a local charge density with the same sign that $\Sigma_\alpha q_\alpha^3 \zeta_\alpha$ near the electrodes. Similarly the electric potential is not zero inside the electrolyte although both plates are grounded: a potential difference builds up between each electrode and the interior of the system. The potential inside the electrolyte has the same sign that $\Sigma_\alpha q_\alpha^3 \zeta_\alpha$.

As possible perspectives to this work let us mention the following. Here we studied the first fluctuations corrections to the mean-field description of the electrolyte. We considered the most simple situation at the mean-field level: both plates are grounded and the mean-field potential is zero everywhere. We choose to study this situation in order to show clearly the effects of fluctuations. However, our method can actually be extended to study more general situations, for example, when a potential difference is imposed between the electrodes. In this case the mean-field description is the Poisson-Boltzmann theory studied by Gouy [1] and Chapman [2], which can be a linear theory if the potential difference is small, or a nonlinear theory if the potential difference is high. On the top of this mean-field description, a generalization of our method can be used to find the corrections due to the micro-ions correlations (whether the mean field is linear or nonlinear).

APPENDIX A: GENERAL EXPRESSION FOR THE DENSITIES

The density can be computed from the grand potential using Eq. (4.1). However, to perform the functional derivative for arbitrary fugacities $\zeta_\alpha(\mathbf{r})$, we should find a more general expression for the grand potential than the one given by Eq. (2.11), which is restricted to constant fugacities satisfying the pseudoneutrality condition (2.1). Similar calculations to the one presented here can also be found in Refs. [25,40,41] in the case of unconfined systems.

In general, the sine-Gordon transformation allows to write the grand partition function without any approximation as [14,24]

$$\Xi = \frac{1}{Z_G} \int \mathcal{D}\phi \, \exp[-S(\phi)], \tag{A1}$$

with Z_G given by Eq. (2.9) and the action S given by

$$S(\phi) = -\int \left[\frac{\beta\varepsilon}{8\pi} \phi(\mathbf{r})\Delta\phi(\mathbf{r}) \right.$$
$$\left. + \sum_\alpha \zeta_\alpha(\mathbf{r}) e^{\beta q_\alpha^2 v^0(\mathbf{r},\mathbf{r})/2} e^{-i\beta q_\alpha \phi(\mathbf{r})} \right] d\mathbf{r}. \tag{A2}$$

Let us define the Gaussian average as

$$\langle \cdots \rangle_G = \frac{1}{Z_G} \int \mathcal{D}\phi(\cdots) e^{-(1/2)\int \phi(\mathbf{r})[-\beta\varepsilon\Delta/4\pi]\phi(\mathbf{r})d\mathbf{r}}. \tag{A3}$$

Notice that the covariance of the preceding functional Gaussian measure is $\langle \phi(\mathbf{r})\phi(\mathbf{r}')\rangle_G = \beta^{-1}v(\mathbf{r},\mathbf{r}')$. Therefore, the last term of Eq. (A2) is very similar to a normal ordering, since by definition

$$:\exp[-i\beta q_\alpha \phi(\mathbf{r})]: = e^{\beta q_\alpha^2 v(\mathbf{r},\mathbf{r})/2} e^{-i\beta q_\alpha \phi(\mathbf{r})}. \tag{A4}$$

However, the important difference is that in Eq. (A2), we subtract the self-energy $v^0(\mathbf{r},\mathbf{r})$ for an unconfined system, not the self-energy $v(\mathbf{r},\mathbf{r})$ for a confined system. As previously mentioned, this has very important physical consequences for confined systems. To proceed, it is natural to define a pseudonormal ordering as

$$:: \exp(-i\beta q_\alpha \phi(r)) :: \; = e^{\beta q_\alpha^2 v_0(\mathbf{r},\mathbf{r})/2} e^{-i\beta q_\alpha \phi(\mathbf{r})} \tag{A5}$$

and to write down the action as

$$S = -\int \left[\frac{\beta\varepsilon}{8\pi}\phi(\mathbf{r})\Delta\phi(\mathbf{r}) + \sum_\alpha \zeta_\alpha(\mathbf{r}) :: e^{-i\beta q_\alpha \phi(\mathbf{r})} :: \right] d\mathbf{r}.$$

$$(A6)$$

As we mentioned in Sec. II, if we use the Coulomb potential v^0 defined by Eq. (2.4), the self-energy $v^0(\mathbf{r},\mathbf{r})$ is infinite. In principle, one should introduce a short-distance cutoff. Without this cutoff, both quantities $e^{-i\beta q_\alpha \phi(\mathbf{r})}$ and $v^0(\mathbf{r},\mathbf{r})$ in Eq. (A5) are not properly defined when taken separately. However, their combination in the definition (A5) of the pseudo-normal ordered exponential $::\exp(-i\beta q_\alpha \phi(\mathbf{r}))::$ is well defined *even* in the case of a vanishing short-distance cutoff. In particular, later on we will proceed to do an expansion of this exponential in powers of $::(-i\beta q_\alpha \phi(\mathbf{r}))^n::$. These quantities are well defined for a vanishing short-distance cutoff and they are of order $(\Gamma_\alpha)^n$ in the Coulombic coupling constant.

For arbitrary position-dependent fugacities the stationary point of the action S is $\phi=-i\psi$ with ψ solution of the mean field Poisson-Boltzmann equation

$$\Delta\psi(\mathbf{r}) + \frac{4\pi}{\varepsilon}\sum_\alpha \zeta_\alpha(\mathbf{r})q_\alpha e^{-\beta q_\alpha \psi(\mathbf{r})} = 0. \quad (A7)$$

Notice that if one takes constant fugacities satisfying the pseudoneutrality condition $\sum_\alpha \zeta_\alpha q_\alpha = 0$, the solution of the mean-field Poisson-Boltzmann equation is simply $\psi(\mathbf{r})=0$.

Let us return to the general case of position-dependent fugacities. Expanding the action to the quadratic order in ϕ around the stationary point leads to $S(-i\psi+\phi)=S_{\mathrm{mf}}+S_1+o(\phi^2)$, with

$$S_{\mathrm{mf}} = S(-i\psi) = \int \left[\frac{\beta\varepsilon}{8\pi}\psi(\mathbf{r})\Delta\psi(\mathbf{r}) - \sum_\alpha \zeta_\alpha(\mathbf{r})e^{-\beta q_\alpha \psi(\mathbf{r})} \right] d\mathbf{r}$$

$$(A8)$$

the action evaluated at the mean-field solution and

$$S_1 = \frac{1}{2}\int \frac{-\beta\varepsilon}{4\pi}\phi(\mathbf{r})\Delta\phi(\mathbf{r})$$
$$+ \sum_\alpha (\beta q_\alpha)^2 \zeta_\alpha(\mathbf{r})e^{-\beta q_\alpha \psi(\mathbf{r})} :: \phi(\mathbf{r})^2 :: d\mathbf{r}. \quad (A9)$$

We can now compute the functional derivative (4.1) with respect to the fugacities to find

$$n_\alpha(\mathbf{r}) = -\frac{\delta S_{\mathrm{mf}}}{\delta\zeta_\alpha(\mathbf{r})} - \frac{\int \mathcal{D}\phi \dfrac{\delta S_1}{\delta\zeta_\alpha(\mathbf{r})} e^{-S_1}}{\int \mathcal{D}\phi e^{-S_1}}. \quad (A10)$$

However, we should take special note of the terms that depend on the mean field $\psi(\mathbf{r})$, since the latter is a function of the fugacities via the Poisson-Boltzmann equation (A7). In particular from Eq. (A7), we have

$$(\Delta_\mathbf{r} - \kappa^2) \left.\frac{\delta\psi(\mathbf{r})}{\delta\zeta_\alpha(\mathbf{r}')}\right|_0 = -\frac{4\pi}{\varepsilon}q_\alpha \delta(\mathbf{r}-\mathbf{r}'), \quad (A11)$$

where $\delta\psi(\mathbf{r})/\delta\zeta_\alpha(\mathbf{r}')|_0$ is evaluated for constant fugacities satisfying the pseudoneutrality condition (2.1) and $\psi(\mathbf{r})=0$. We can then write

$$\left.\frac{\delta\psi(\mathbf{r})}{\delta\zeta_\alpha(\mathbf{r}')}\right|_0 = q_\alpha v_{\mathrm{DH}}(\mathbf{r},\mathbf{r}'), \quad (A12)$$

with $v_{\mathrm{DH}}(\mathbf{r},\mathbf{r}')$ the DH potential satisfying the DH equation (4.3) and the imposed boundary conditions. Taking this into account, we find the required functional derivatives evaluated at constant fugacities satisfying Eq. (2.1) and $\psi(\mathbf{r})=0$, as

$$\left.\frac{\delta S_{\mathrm{mf}}}{\delta\zeta_\alpha(\mathbf{r})}\right|_0 = -1 \quad (A13)$$

and

$$\left.\frac{\delta S_1}{\delta\zeta_\alpha(\mathbf{r})}\right|_0 = \frac{(\beta q_\alpha)^2}{2} :: \phi(\mathbf{r})^2 ::$$
$$- \frac{\beta^3 q_\alpha}{2}\sum_\gamma q_\gamma^3 \zeta_\gamma \int v_{\mathrm{DH}}(\mathbf{r}',\mathbf{r}) :: \phi(\mathbf{r})^2 :: d\mathbf{r}.$$

$$(A14)$$

For constant fugacities, the action S_1 reduces to

$$S_1|_0 = \frac{1}{2}\int \frac{-\beta\varepsilon}{4\pi}\phi(\mathbf{r})\Delta\phi(\mathbf{r}) + \sum_\gamma (\beta q_\gamma)^2 \zeta_\gamma :: \phi(\mathbf{r})^2 :: d\mathbf{r}.$$

$$(A15)$$

If we define the average

$$\langle\cdots\rangle_{\mathrm{DH}} = \frac{\int \mathcal{D}\phi(\cdots)e^{-S_1|_0}}{\int \mathcal{D}\phi e^{-S_1|_0}}, \quad (A16)$$

we have

$$\beta\langle::\phi(\mathbf{r})^2::\rangle_{\mathrm{DH}} = v_{\mathrm{DH}}(\mathbf{r},\mathbf{r}) - v^0(\mathbf{r},\mathbf{r}). \quad (A17)$$

Replacing (A13) and (A14) into Eq. (A10) and using (A17) gives Eq. (4.2) for the densities.

APPENDIX B: ON THE IMPORTANCE OF THE BOUNDARY CONDITIONS

As was mentioned in Sec. III, there is an important difference on the behavior of the disjoining pressure in the case with ideal conductor boundaries and the case when the electrolyte is confined by a walls made of material with a dielectric constant ε_w [31]. Namely, for the latter case, the pressure has an exponential decay $e^{-2\kappa W}$ at large separations W, whereas in the case presented here we found an algebraic decay in $1/W^3$, which is, furthermore, universal (i.e., independent of the microscopic detail): notice that the coefficient of W^{-3} in Eq. (3.8) is just a number independent of the De-

bye length κ^{-1} and of the other microscopic parameters.

Although the ideal boundary conditions case considered here is formally obtained when $\varepsilon_w = \infty$, this limit has a very different behavior than in the case $0 < \varepsilon_w < \infty$ [the ideal dielectric boundaries case, $\varepsilon_w = 0$, is also special, in that case there is also an algebraic decay at large separations W^{-3} in the pressure [42] similar to the one found here]. This difference is not only present in the behavior of the pressure, but also in the correlation functions. For instance, it is known that for dielectric boundaries with $0 < \varepsilon_w < \infty$, the charge correlation along the walls have an algebraic decay as $|\mathbf{r}_\perp|^{-3}$, where $\mathbf{r}_\perp$ is the direction parallel to the walls [43,44], whereas for ideal conductor boundaries $\varepsilon_w = \infty$ (or ideal dielectric $\varepsilon_w = 0$) this decay is faster that any power law (see the review Ref. [45] and references cited therein).

In this appendix, we show how both kinds of boundary conditions can be related, and understand the presence of the universal term in $1/W^3$ in the Dirichlet boundary conditions case and its absence in the case of insulating boundaries without image forces. The following analysis relies on a macroscopic description of the electrolyte in terms of collective modes, which actually disregards the microscopic detail of the system, but can give a correct description of some universal properties of the system for instance the presence of the $1/W^3$ term in the pressure.

Let us consider an electrolyte confined in the slab domain D with separation W and with insulating void boundaries. For simplicity and without loss of generality, we will take the dielectric constant of the solvent $\varepsilon = 1$. It is well known that the electric potential Φ of a linear collective mode of oscillation with frequency ω of this electrolyte can be described by a Laplace type of equation

$$\chi_\omega \Delta \Phi = 0 \tag{B1}$$

inside the domain D, with an effective dielectric constant $\chi_\omega = 1 - \omega_p^2/\omega^2$ and where ω_p is the plasma frequency (see, for instance, [46]). Outside the domain where the electrolyte is confined, Φ satisfies a Laplace equation $\Delta \Phi = 0$ since there are no real charges outside. The potential should also satisfy the boundary conditions $\Phi_{in} = \Phi_{out}$ and $\partial_n \Phi_{out} = \chi_\omega \partial_n \Phi_{in}$, where $\partial_n \Phi$ denotes the component of (minus) the electric field normal to the boundary.

One can distinguish between two type of modes. If $\chi_\omega \neq 0$, Φ has a vanishing Laplacian inside the domain, there are no charges inside the domain. Only at the boundaries are there some surface charges. These are the surface modes. They represent a system of two parallel walls in the vacuum with fluctuating surface charges. Thus, the contribution of the surface modes to the pressure is the same as the one of the Lifshitz theory [34] in the classical (i.e., nonquantum) limit [47,48]. This contribution comes from the well-known Casimir forces, it is attractive and for large separations, it is given by $-k_B T \zeta(3)/(8\pi W^3)$.

If $\omega = \omega_p$, $\chi_\omega = 0$ and charges inside the domain can exist since $\Delta \Phi \neq 0$ inside D is acceptable. These are the volume modes that oscillate all at the same frequency $\omega = \omega_p$, the plasma frequency. Due to the boundary conditions, the potential for volume modes satisfy Neumann boundary conditions outside the domain $\partial_n \Phi_{out} = 0$, and since Φ is harmonic outside and vanishes at infinity, this implies that $\Phi = 0$ everywhere outside the domain D. In conclusion, the volume modes represent a system of volume charges that satisfy Dirichlet boundary conditions for the potential. The volume modes of the electrolyte confined by insulating void boundaries are very similar to the system we studied here with ideal conductor boundaries. If one computes the contribution to the pressure coming from these volume modes, one will find the same result as the one we have found in Sec. III A, namely, that the pressure has an universal algebraic decay for large separations W given by $+k_B T \zeta(3)/(8\pi W^3)$. This contribution gives a repulsive force and is exactly the opposite as the one coming from the surface modes.

Adding both contributions from the surface and the volume modes, one finds that the algebraic contributions to the pressure cancel each other. In conclusion for the system confined by insulating void boundaries there is no term in $1/W^3$ in the pressure as previously noted [31]. However, for ideal conductor boundary conditions, a repulsive term in $1/W^3$ for the pressure is present.

The above analysis is somehow similar to the one done in the comparison between ideal conductor and good conductor model, in the sense that the absence of the $1/W^3$ algebraic term in the pressure in the insulating void boundaries case and the good conductor case is due to a cancellation between the Lifshitz term and the one from the ideal conductor model. However, the specific details are different.

---

[1] G. Gouy, J. Phys. (France) **IX**, 457 (1910).

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

[3] E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, New York, 1948);Dover, New York, 1999).

[4] See, e.g., D. A. McQuarrie, *Statistical Mechanics*, Harper Collins, New York, 1976).

[5] S. Levine and G. P. Dube, Trans. Faraday Soc. **35**, 1125 (1939).

[6] A. M. Larsen and D. G. Grier, Nature (London) **385**, 230 (1997).

[7] G. M. Kepler and S. Fraden, Phys. Rev. Lett. **73**, 356 (1994).

[8] M. D. Carbajal-Tinoco, F. Castro-Román, and J. L. Arauz-Lara, Phys. Rev. E **53**, 3745 (1996).

[9] J. C. Neu, Phys. Rev. Lett. **82**, 1072 (1999).

[10] J. E. Sader and D. Y. Chan, Langmuir **16**, 324 (2000).

[11] E. Trizac and J.-L. Raimbault, Phys. Rev. E **60**, 6530 (1999).

[12] E. Trizac, Phys. Rev. E **62**, R1465 (2000).

[13] T. Brandes and L. Lue, cond-mat/0311375v1.

[14] A. Torres and G. Téllez, J. Phys. A **37**, 2121 (2004).

[15] B. Jancovici and G. Téllez, J. Phys. A **29**, 1155 (1996).

[16] J.-N. Aqua and F. Cornu, J. Stat. Phys. **105**, 211 (2001).

[17] J.-N. Aqua and F. Cornu, J. Stat. Phys. **105**, 245 (2001).

[18] J.-N. Aqua, Ph.D. thesis, Université de Paris XI, 2000.

[19] J. L. Lebowitz and E. Lieb, Phys. Rev. Lett. **22**, 631 (1969).

[20] E. Lieb and J. L. Lebowitz, Adv. Math. **9**, 316 (1972).

[21] A. Alastuey, B. Jancovici, L. Blum, P. J. Forrester, and M. L. Rosinberg, J. Chem. Phys. **83**, 2366 (1985).

[22] T. Kennedy, Commun. Math. Phys. **92**, 269 (1983).

[23] A. Torres and G. Téllez, e-print cond-mat/0404588.

[24] S. Samuel, Phys. Rev. D **18**, 1916 (1978).

[25] J. M. Caillol, J. Stat. Phys. **115**, 1483 (2004).

[26] J. L. Lebowitz and Ph. A. Martin, J. Stat. Phys. **34**, 287 (1984).

[27] B. Jancovici, J. Stat. Phys. **80**, 445 (1995).

[28] S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1965).

[29] L. Šamaj and B. Jancovici, J. Stat. Phys. **103**, 717 (2001).

[30] B. Jancovici and G. Téllez, J. Stat. Phys. **82**, 609 (1996).

[31] P. Attard, D. J. Mitchell, and B. W. Ninham, J. Chem. Phys. **88**, 4978 (1988).

[32] D. S. Dean and R. R. Horgan, e-print cond-mat/0403150.

[33] L. Merchán and G. Téllez, J. Stat. Phys. **114**, 735 (2004).

[34] E. M. Lifshitz, Sov. Phys. JETP **2**, 73 (1956).

[35] G. S. Manning, J. Chem. Phys. **51**, 924 (1969).

[36] S. Alexander, P. M. Chaikin, P. Grant, G. J. Morales, and P. Pincus, J. Chem. Phys. **80**, 5776 (1984).

[37] G. Téllez and E. Trizac, Phys. Rev. E **70**, 011404 (2004).

[38] D. C. Grahame, J. Chem. Phys. **21**, 1054 (1953).

[39] J. Ulander, H. Greberg, and R. Kjellander, J. Chem. Phys. **115**, 7144 (2001).

[40] J. M. Caillol and J. L. Raimbault, J. Stat. Phys. **103**, 753 (2001).

[41] J. L. Raimbault and J. M. Caillol, J. Stat. Phys. **103**, 777 (2001).

[42] B. Jancovici and L. Šamaj, J. Stat. Phys. **104**, 755 (2001).

[43] B. Jancovici, J. Stat. Phys. **29**, 263 (1982).

[44] J.-N. Aqua and F. Cornu, Phys. Rev. E **68**, 026133 (2003).

[45] Ph. A. Martin, Rev. Mod. Phys. **60**, 1075 (1988).

[46] G. Téllez, Phys. Rev. E **55**, 3400 (1997).

[47] P. J. Forrester, B. Jancovici, and G. Téllez, J. Stat. Phys. **84**, 359 (1996).

[48] Y. Levin, Physica A **265**, 432 (1999).