Classical charged fluids at equilibrium near an interface: Exact analytical density profiles and surface tension

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Abstract. The structure of equilibrium density profiles in an electrolyte in the vicinity of an interface with an insulating or conductive medium is of crucial importance in chemical physics and colloidal science. The Coulomb interaction is responsible for screening effects, and in dilute solutions the latter effects give rise to universal leading corrections to nonideality, which distinguish electrolyte from nonelectrolyte solutions. An example is provided by the excess surface tension for an air–water interface, which is determined by the excess particle density, and which was first calculated by Onsager and Samaras. Because of the discrepancy between the dielectric constants on both sides of the interface, every charge in the electrolyte interacts with an electrostatic image, and the Boltzmann factor associated with the corresponding self-energy has an essential singularity over the length scale l from the wall. Besides Coulomb interactions, short-range repulsions must be taken into account in order to prevent the collapse between charges with opposite signs or between each charge and its image when the solvent dielectric constant is lower than that of the continuous medium on the other side of the interface. For a dilute and weakly-coupled electrolyte, l is negligible with respect to the bulk Debye screening length ξ_{D}. In the framework of the grand-canonical ensemble, systematic partial resummations in Mayer diagrammatics allow one to exhibit that, in this regime, the exact density profiles at leading order are the same as if they were calculated in a partially-linearized mean-field theory, where the screened pair interaction obeys an inhomogeneous Debye equation. In the latter equation the effective screening length depends on the distance x from the interface: it varies very fast over the length l and tends to its bulk value over a few ξ_{D}s. The equation can be solved iteratively at any distance x, and the exact density profiles are calculated analytically up to first order in the coupling parameter l/ξ_{D}. They show the interplay between three effects: (1) the geometric repulsion from the interface associated with the deformation of screening clouds, (2) the polarization effects described by the images on the other side of the interface, (3) the interaction between each charge and the potential drop created by the electric layer which appears as soon as the fluid has not a charge-symmetric composition. Moreover, the expressions allow us to go beyond Onsager–Samaras theory: the surface tension is calculated for charge-asymmetric electrolytes and for any value of the ratio between the dielectric constants on both sides of the interface. Similar diagrammatic techniques also allow one to investigate the charge renormalization in the dipolar effective pair interaction along the interface with an insulating medium.

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1. Introduction

The study of electrolyte solutions has been an important part of chemical physics throughout its history, in electrochemistry as well as in colloid chemistry. The long-range Coulomb interaction causes special screening mechanisms, and, in dilute solutions, the screening effects give rise to universal leading corrections to nonideality, which distinguish electrolyte from nonelectrolyte solutions. The limiting laws, such as that for the excess pressure in the bulk, are universal in the sense that they depend only on the valence type of the salt and on the macroscopic characterization of the solvent.

In the theory of surface properties of dilute electrolyte solutions, an example of these laws appears in the case of the excess surface tension. In the first experiments on aqueous liquid–vapor interfaces, the measured surface tensions of electrolyte solutions were larger than those of pure solvents, which signaled a negative adsorption of ions, according to the Gibbs adsorption equation. Since the salt concentration in the vapor phase is exceedingly small (far from the critical point of the liquid–vapor transition), the air can be mimicked by an impenetrable wall. In 1924, Wagner [1] produced a phenomenological theory in the spirit of the linearized Poisson–Boltzmann theory introduced by Gouy [2] and Debye and Hückel [3]; he argued that the ion depletion mainly stemmed from the repulsion of all ion species from the interface, due to the electrostatic interaction with the images, which arises from the discrepancy between the dielectric constants on both sides of the interface. Wagner considered only the case of symmetric $Z{:}Z$ electrolytes and he assumed, as a first approximation, that the ratio between the dielectric constants of air and water could be set to zero, i.e., $D_{\mathrm{air}}/D_{\mathrm{water}} = 0$. However, even in his mean-field theory, the screened interaction between two ions obeys an inhomogeneous Debye equation, where the screening length ξ depends on the distance x from the wall through the density profiles. The latter vary very fast in the vicinity of the wall, because the self-image interaction diverges in the vicinity of the interface as $1/x$, and its Boltzmann factor cannot be treated perturbatively. Wagner was not able to obtain an analytical expression for the density profiles, and he only calculated the surface tension by numerical integrations.

In 1934, Onsager and Samaras [4] simplified Wagner's phenomenological theory and first calculated the analytical expression of the density profiles. They just avoided the technical difficulty in the resolution of the problem, namely the dependence of the screening length ξ upon the distance x from the wall in the generalized Debye equation. They replaced $\xi(x)$ by the value it takes for distances larger than the Debye bulk screening length, and they argued that the corresponding error in the excess surface tension was indeed a higher-order correction at low densities. They found a positive leading correction proportional to $\rho[-\ln\rho + C^{\mathrm{st}}]$, independent of the short-range interactions.

In the present paper, we consider electrolytes which are not necessarily charge-symmetric and for any value of the ratio between the dielectric constants on both sides of the interface. We give the exact analytical expression for the density profiles in a high-dilution scaling regime [5,6], and we control the structure of the corrections to the leading terms. Moreover, the dependence upon the closest approach distance to the wall b is controlled in various scaling limits. This enables us to get an extension of the Onsager–Samaras formulas for the density profiles and the surface tension, and to determine their *a priori* domain of validity.

The paper is organized as follows: The model for the electrolyte and the interface is introduced in §2. A few basic aspects of screening in the bulk are summarized in §3. The resolution method and the structure of the exact analytical profiles are presented in §4. The interplay between the steric deformation of screening clouds and polarization effects is analysed in §5. Effects in competition in the density profiles and their relation to screening mechanisms are discussed in §6. Finally, in §7, the surface tension is written for the first time for a generic electrolyte and an interface with an electrostatic response which may be either repulsive or attractive.

2. Model for the electrolyte and the wall

The impenetrable wall in the region $x < 0$ is only characterized by its dielectric constant D_{w}, whereas the electrolyte is described by the usual primitive model [7] in the framework of classical statistical mechanics. Every charged particle of the species α is represented as a point charge which sits at the center of a hard sphere with diameter σ_α. The net bare solvated charge is written as $e_\alpha \equiv Z_\alpha e$, where e is the absolute value of the electron charge and Z_α may be positive or negative. The solvent is modelled as a continuous medium with a uniform dielectric constant D_{s}. Moreover, for the sake of simplicity, the excluded-volume sphere of every particle is assumed to be made of a material with the same dielectric constant as that of the solvent. Therefore, the Coulomb potential $e_\alpha v(\mathbf{r}, \mathbf{r}')$ created at any point $\mathbf{r}'$ by a charge e_α located at the center $\mathbf{r}$ of a hard-sphere obeys the Poisson equation,

$$\Delta_{\mathbf{r}'} v(\mathbf{r}, \mathbf{r}') = -\frac{4\pi}{D_{\mathrm{s}}} \delta(\mathbf{r} - \mathbf{r}'), \tag{1}$$

with the appropriate electrostatic boundary conditions.

2.1 *Polarization*

In the bulk, the solution is

$$v_{\mathrm{B}}(\mathbf{r}, \mathbf{r}') = \frac{1}{D_{\mathrm{s}}|\mathbf{r} - \mathbf{r}'|}. \tag{2}$$

In the vicinity of the interface, since there is a medium with a dielectric constant D_{w} on the left side of the plane $x = 0$, the solution of the Poisson equation (1) for $x > 0$ and $x' > 0$ reads

$$v(\mathbf{r}, \mathbf{r}') = \frac{1}{D_{\mathrm{s}}} \left[\frac{1}{|\mathbf{r} - \mathbf{r}'|} - \Delta_{\mathrm{el}} \frac{1}{|\mathbf{r}^\star - \mathbf{r}'|} \right] \quad \text{with} \quad \Delta_{\mathrm{el}} \equiv \frac{D_{\mathrm{w}} - D_{\mathrm{s}}}{D_{\mathrm{w}} + D_{\mathrm{s}}}. \tag{3}$$

In (3), $\mathbf{r}^\star$ is the point symmetric to $\mathbf{r}$ with respect to the plane $x = 0$ and Δ_{el} measures the difference between the dielectric constants on both sides of the interface. A charge in the solvent induces a polarization charge density inside the other medium in the wall. In the present plane geometry, by virtue of (3), the Coulomb potential $e_\alpha v(\mathbf{r}, \mathbf{r}')$ that a charge e_α at $\mathbf{r}$ creates at point $\mathbf{r}'$ can be seen as the sum of the bulk potential $e_\alpha v_{\mathrm{B}}(\mathbf{r}, \mathbf{r}')$ and the bulk potential which would be created at $\mathbf{r}'$ by a charge $-\Delta_{\mathrm{el}} e_\alpha$ at $\mathbf{r}^\star$ inside the wall, if the latter had the same dielectric constant as the solvent [8].

2.2 *Strong inhomogeneity due to the self-image interaction*

When $D_{\mathrm{w}} \neq D_{\mathrm{s}}$, the total electrostatic potential energy of the system involves several kinds of contributions which can be rewritten in terms of the bulk Coulomb interaction: each charge interacts through the bulk Coulomb potential not only with the other charges in the electrolyte and their images, but also with its own image. The latter self-image interaction corresponds to an external potential proportional to e_α^2, or it can be viewed as a self-energy,

$$e_\alpha^2 V_{\mathrm{self}}(x) \equiv \frac{e_\alpha^2}{2} [v - v_{\mathrm{B}}](\mathbf{r}, \mathbf{r}') \Big|_{\mathbf{r}=\mathbf{r}'} = -\Delta_{\mathrm{el}} \frac{e_\alpha^2}{2 D_{\mathrm{S}}} \frac{1}{2x}. \tag{4}$$

If charges did not interact with each other but only with their self images, then the density profiles would be $\rho_{\mathrm{self},\alpha}^{\mathrm{bare}}(x) = \rho_\alpha^{\mathrm{B}} \exp[-\beta e_\alpha^2 V_{\mathrm{self}}(x)]$.

As a consequence, if $D_{\mathrm{w}} < 1$, the wall is electrostatically repulsive, and $\rho_{\mathrm{self},\alpha}^{\mathrm{bare}}(x)$ vanishes with an essential singularity as x goes to zero. If $D_{\mathrm{w}} > 1$, the wall is electrostatically attractive and the divergence of the self-image interaction in the vicinity of the wall makes $\rho_{\mathrm{self},\alpha}^{\mathrm{bare}}(x)$ explode when x goes to zero. Therefore, in order to prevent the collapse onto the wall, the closest approach distance of each particle to the wall cannot be set to zero in various integrals. The latter distance may be determined by the ions' excluded-volume spheres or by a monolayer of adsorbed molecules on the interface, for instance water molecules in the case of an aqueous–mercury interface [9]. For the sake of simplicity, it is chosen to have the same value b for all species, as it is indeed the case in the second mechanism responsible for it. In order to trace the excluded-volume effect at contact with the interface, we consider a finite b even for $\Delta_{\mathrm{el}} \leq 1$, but in the latter case one is allowed to take the limit where b becomes negligible with respect to all other length scales and to set $b = 0$.

3. Screening in the bulk

3.1 *Neutrality sum rules*

In the bulk, translational invariance implies that, at equilibrium, the bulk densities ρ_α^{B} are uniform and the macroscopic electrostatic field vanishes [10]. Therefore the n_s bulk densities obey the local neutrality relation

$$\sum_{\alpha=1}^{n_s} e_\alpha \rho_\alpha^{\mathrm{B}} = 0. \tag{5}$$

Another basic screening rule in the bulk is that the set made by a charge and its screening cloud is neutral [10],

$$\int d\mathbf{r} \sum_{\gamma} e_{\gamma} \rho_{\gamma}^{\mathrm{B}} h(e_{\alpha}, \mathbf{r}_0; e_{\gamma}, \mathbf{r}) = -e_{\alpha}. \tag{6}$$

$h(e_{\alpha}, \mathbf{r}_0; e_{\gamma}, \mathbf{r})$ denotes the probability of finding a charge e_{γ} at point $\mathbf{r}$ given that a charge e_{α} sits at position $\mathbf{r}_0$ minus 1. We stress that there are other screening sum rules about $h(e_{\alpha}, \mathbf{r}_0; e_{\gamma}, \mathbf{r})$ and various correlations [10]. None of them involves explicitly the short-range repulsion which must be introduced in order to avoid the collapse of the classical fluid because of the attraction between charges with opposite signs.

3.2 *Debye approximation for point charges*

In the Debye approximation, which is a linearized Poisson–Boltzmann theory, and in the limit where the radii of the excluded-volume spheres vanish, the bulk correlation between a charge e_{α} and a charge e_{γ} in its screening cloud reads

$$h_{\mathrm{D}}(e_{\alpha}, \mathbf{r}_0; e_{\gamma}, \mathbf{r}) = -\beta e_{\alpha} e_{\gamma} \phi_{\mathrm{D}}(\mathbf{r}_0, \mathbf{r}). \tag{7}$$

By the definition of ϕ_{D}, $\delta q \delta q' \phi_{\mathrm{D}}$ is the immersion free energy between two infinitesimal external point charges δq and $\delta q'$ calculated in the framework of the linear-response theory as if the radii of the excluded-volume spheres of the fluid charges were equal to zero. ϕ_{D} is the solution of the Debye equation with electrostatic boundary conditions,

$$[\Delta_{\mathbf{r}} - \kappa_{\mathrm{D}}^2]\phi_{\mathrm{D}}(\mathbf{r} - \mathbf{r}_0) = -\frac{4\pi}{D_{\mathrm{s}}}\delta(\mathbf{r} - \mathbf{r}_0) \quad \text{with} \quad \kappa_{\mathrm{D}} \equiv \sqrt{\frac{4\pi\beta}{D_{\mathrm{s}}}\sum_{\alpha=1}^{n_s}\rho_{\alpha}^{\mathrm{B}}e_{\alpha}^2}, \tag{8}$$

at the inverse temperature $\beta = 1/(k_{\mathrm{B}}T)$, where k_{B} is the Boltzmann constant and T is the absolute temperature. The Debye interaction ϕ_{D} reads

$$\phi_{\mathrm{D}}(\mathbf{r} - \mathbf{r}_0) = \frac{e^{-\kappa_{\mathrm{D}}|\mathbf{r}-\mathbf{r}_0|}}{D_{\mathrm{s}}|\mathbf{r} - \mathbf{r}_0|}. \tag{9}$$

In fact, the Debye approximation already fulfills the internal-screening rule (6). The reason is that the Debye correlation becomes exact in some high-dilution scaling regimes [11].

3.3 *High-dilution 'Debye' scaling regimes and universal laws*

If the solution is diluted, the Coulomb coupling between charges of any species separated by the mean interparticle distance a is weak: the condition of low densities,

$(\sigma/a)^3 \ll 1$, where σ is the mean ion diameter, implies that the coupling parameter $\Gamma \equiv \beta e^2/(D_s a)$ is such that $\Gamma^3 \ll 1$, if the temperature is high enough for $\beta e^2/(D_s \sigma)$ to be of unit order or far smaller than 1. Then, for a generic quantity, a double-expansion in the parameters σ/a and Γ can be performed systematically from the exact resummed Mayer diagrammatics first introduced for bulk correlations by Meeron [12], and which is valid for any peculiar form of an additive short-range repulsive interaction. The expansion of the integral of the correlation starts by a term of order $\Gamma^{3/2}$ and contributions of the form (see [13]),

$$\left(\frac{\sigma}{a}\right)^3, \quad \left(\frac{\sigma}{a}\right)^2 \Gamma, \quad \frac{\sigma}{a}\Gamma^2, \quad \Gamma^3, \quad \Gamma^3 \ln\left[\left(\frac{\sigma}{a}\right)^2 \Gamma\right], \quad \text{and} \quad \Gamma^3 f\left(\frac{\beta e^2}{D_s \sigma}\right), \qquad (10)$$

where $\beta e^2/(D_s \sigma) = \Gamma/(\sigma/a)$ and $f(u)$ is of order u when u goes to zero. In fact, the term of order $\Gamma^{3/2}$ comes from the point-charge Debye screened interaction (9) to the correlation.

Therefore, in various integrals, the Debye approximation (7) for the correlation $h(e_\alpha, \mathbf{r}_0; e_\gamma, \mathbf{r})$ gives the exact leading correction to the ideal contribution in scaling regimes of temperature and density [13], where

$$\left(\frac{\sigma}{a}\right)^3 \ll \varepsilon \equiv \frac{1}{2}\kappa_D \beta \frac{e^2}{D_s} \ll 1, \qquad (11)$$

with $\varepsilon \propto \Gamma^{3/2}$. The scaling regimes correspond to two different kinds of expansions in the density and temperature parameters. In regime (1), the density vanishes at fixed temperature; then $\beta e^2/(D_s \sigma)$ is also fixed, i.e., $(\sigma/a)^3 \propto \varepsilon^2$, and all contributions in (10) are of order ε^2 or $\varepsilon^2 \ln \varepsilon$. In regime (2), the density vanishes while the temperature goes to infinity, but not too fast in order to ensure that $(\sigma/a)^3 \ll \varepsilon$; then $\beta e^2/(D_s \sigma)$ also vanishes, i.e., $\varepsilon^2 \ll (\sigma/a)^3$, and in (10) the contributions different from the $(\sigma/a)^3$ term are in fact of higher order, $(\sigma/a)^3$ times a function of $\beta e^2/(D_s \sigma)$, which vanishes when $\beta e^2/(D_s \sigma)$ goes to zero. In the following, expansions performed in the regimes where inequality (11) holds will be called ε-expansions.

As a consequence, the universal corrections to nonideality governed by screening effects in very dilute electrolytic solutions are described by the Debye theory in scaling regimes (11). For instance, the excess pressure in the bulk is given by the limit law,

$$\beta P^B - \sum_{\alpha}^{n_s} \rho_\alpha^B = -\frac{\kappa_D^3}{24\pi} + \mathcal{O}(\rho\varepsilon^2), \qquad (12)$$

where κ_D^3 is a term of order $\rho\varepsilon$, and $\mathcal{O}(\rho\varepsilon^2)$ denotes both terms of order $\rho\varepsilon^2$ (times a possible $\ln \varepsilon$) and other terms of the form (10) which are negligible with respect to ε in high-dilution regimes (11). All these terms have been calculated in a systematic approach by Haga [14,14a]. We notice that the steric factor $\exp(\kappa_D \sigma)/[1 + \kappa_D \sigma]$, which multiplied ϕ_D (9) in the original Debye–Hückel screened interaction, yields corrections to the excess pressure only from relative order $\varepsilon \times (\kappa_D \sigma)$ [11]. Since $\varepsilon \times (\kappa_D \sigma) \propto \Gamma^2(\sigma/a)$, it is only one among the contributions (10). In regime (1) it is of order ε^2, and in regime (2) it is negligible with respect to the $(\sigma/a)^3$ correction.

4. Density profiles near the wall

4.1 *Onsager–Samaras theory*

Onsager and Samaras consider an interface in the approximation $\Delta_{\mathrm{el}} = -1$ and a symmetric $Z{:}Z$ electrolyte, where charges are Ze and $-Ze$. Then, $\rho_+^{\mathrm{B}} = \rho_-^{\mathrm{B}} = \rho^{\mathrm{B}}$, by virtue of the bulk local neutrality (5). In their heuristic approach, they solve the Debye equation (8) with a constant κ_{D} for all $x > 0$ and with the electrostatic boundary conditions for $\Delta_{\mathrm{el}} = -1$. The solution $\phi_{\mathrm{D}}(\mathbf{r}_0 - \mathbf{r}) + \phi_{\mathrm{D}}(\mathbf{r}_0^\star - \mathbf{r})$ yields a phenomenological screened self-energy, and they write

$$\rho_+(x) = \rho_-(x) = \rho^{\mathrm{B}} \exp\!\left[-\beta \frac{Z^2 e^2}{2D_{\mathrm{S}}} \frac{\mathrm{e}^{-2\kappa_{\mathrm{D}} x}}{2x} \right] \quad \text{for} \quad \Delta_{\mathrm{el}} = -1. \qquad (13)$$

In other words, they assume that the effect of pair Coulomb interactions upon the bare density profiles $\rho_{\mathrm{self},\alpha}^{\mathrm{bare}}(x)$ (see (4)) is just to multiply the bare Coulomb interaction $e_\alpha^2 V_{\mathrm{self}}(x)$ of each charge with its image by the bulk Debye screening factor $\exp(-2\kappa_{\mathrm{D}} x)$ for two charges separated by a distance $2x$.

From the expression for the density profiles, Onsager and Samaras calculate the universal contribution to the difference $\Delta\gamma$ between the surface tension of the electrolyte solution and that of the pure solvent. They find if $\Delta_{\mathrm{el}} = -1$ and $\kappa_{\mathrm{D}} b = 0$,

$$\beta \Delta\gamma_{\mathrm{OS}}^{(0)} = \frac{\kappa_{\mathrm{D}}^2}{16\pi} \left[-\ln\!\left(\frac{\beta Z^2 e^2 \kappa_{\mathrm{D}}}{2D_{\mathrm{S}}} \right) - 2C + \frac{3}{2} \right], \qquad (14)$$

where C is the Euler constant, $C = 0.577215\ldots$. $\Delta\gamma_{\mathrm{OS}}^{(0)}$ in (14) is positive, since $Z^2\varepsilon \ll 1$.

In fact, though they set b equal to zero in the lower bound of the integral of the density profile in the calculation of the excess surface tension, as if the ion diameter were negligible, Onsager and Samaras introduce the effect of the ion diameter σ in the bulk-screened self-image interaction, as it was described in the original Debye–Hückel theory (see the end of §3.3), and they calculate the corresponding steric corrections to $\Delta\gamma_{\mathrm{OS}}^{(0)}$. These corrections start at relative order $(\kappa_{\mathrm{D}}\sigma)^2 \propto \Gamma(\sigma/a)^2$, whereas other contributions from the interplay between the excluded-volume effects and Coulomb interactions (see (11)) also arise at the same order in regime (1) and even at lower order $(\sigma/a)^3$ in regime (2).

4.2 *Systematic method*

In our method, we consider Mayer diagrams for the fugacity expansions of the densities: the generalized fugacity at point x involves the Boltzmann factor of the self-image energy and that of the short-range repulsion from the wall, while the Mayer bond takes the hard-core repulsive pair interaction into account. Exact systematic partial resummations are performed in two steps [6]. The first step describes the screening of the electrostatic self-energy: it introduces a screened fugacity (with a screened self-energy $V_{\mathrm{self},1}^{\mathrm{sc}}(x)$ in it) associated with a screened potential $\phi_1(x, x', \mathbf{y})$ (where $\mathbf{y}$ is the projection of $\mathbf{r} - \mathbf{r}'$ onto the plane of the

interface). ϕ_1 obeys a Debye equation (see (8)) with an effective screening length κ_1^{-1} which depends on the distance x from the wall,

$$[\Delta_{\mathbf{r}} - \kappa_1^2(x)]\phi_1(\mathbf{r}', \mathbf{r}) = -\frac{4\pi}{D_{\mathrm{S}}}\delta(\mathbf{r} - \mathbf{r}') \tag{15}$$

with

$$\kappa_1^2(x) \equiv \frac{4\pi\beta}{D_{\mathrm{S}}}\sum_{\alpha=1}^{n_s} e_\alpha^2 z_\alpha \exp\left[-\beta e_\alpha^2 V_{\mathrm{self}}(x)\right]. \tag{16}$$

After a second step, which exhibits the screening of pair interactions, there appear another screened fugacity and another screened potential ϕ_2, which obeys eq. (15) with another $\kappa_2(x)$, which involves the screened fugacity at step 1, $V_{\mathrm{self},1}^{\mathrm{sc}}(x)$. The latter decays exponentially at large distances, but still varies as $1/x$ in the vicinity of the wall.

The main difficulty is then to handle equations such as (15), where $\kappa_i^2(x)$ ($i = 1$ or 2) varies drastically over the length scale $\beta e^2/D_{\mathrm{S}}$: in the case of an electrostatically repulsive wall ($\Delta_{\mathrm{el}} < 0$), $\kappa_i^2(x)$ vanishes with an essential singularity, whereas in the case of an electrostatically attractive wall ($\Delta_{\mathrm{el}} > 1$), it diverges when x goes to zero. In ref. [6] a formal series representation was devised for the solution $\phi_i(x, x', \mathbf{y})$ of a generic inhomogeneous Debye equation (15) with any function $\kappa_i^2(x)$ that tends to a non-zero value when x goes to $+\infty$. It enables one to perform a systematic expansion in powers of the ratio of the length scale over which $\kappa_i(x)$ varies in the vicinity of the wall and its limit value far away from the wall. At every order the expansion is valid for any distance x. It can be viewed as the result of an iterative method for the resolution of the equation. In the present case, the length-scale ratio is just that between the range of the self-image interaction and the bulk screening Debye length, namely the parameter ε (up to a numerical factor).

The expansions are performed in the parameters ε, $(\sigma/a)^3$ in the two regimes which fulfill (11). Moreover, in these regimes $\kappa_{\mathrm{D}}b \ll 1$ (see ref. [13]), and expansions in powers of $\kappa_{\mathrm{D}}b$ must also be done. Indeed, if bulk densities vanish at fixed temperature,

$$\left(\frac{\sigma}{a}\right)^3 \propto \varepsilon^2 \quad \text{and} \quad \kappa_{\mathrm{D}}b \propto \varepsilon \quad \text{(regime (1))}. \tag{17}$$

If bulk densities vanish while the temperature goes to infinity, but not too fast in order to ensure that $(\sigma/a)^3 \ll \varepsilon$, then

$$\varepsilon^2 \ll \left(\frac{\sigma}{a}\right)^3 \ll \varepsilon \ll \kappa_{\mathrm{D}}b \ll 1 \quad \text{(regime (2))}. \tag{18}$$

In regime (1) double-expansions of functions of ε and $\kappa_{\mathrm{D}}b$ are performed at fixed $\varepsilon/(\kappa_{\mathrm{D}}b)$, whereas the corresponding expansions in regime (2) are derived from those in regime (1) by taking the limit $\varepsilon/(\kappa_{\mathrm{D}}b) = 0$ at fixed $\kappa_{\mathrm{D}}b$.

4.3 *Exact analytical density profiles in the high-dilution scaling regimes*

Eventually, the exact density profiles up to order ε (see definition at the end of §3.3) prove to be the same ones as if the first equation of the exact BGY (Born–Green–

Yvon) hierarchy had been solved in the partially-linearized mean-field scheme devised in ref. [5]. For the sake of pedagogy, we write the first BGY equation (see e.g. ref. [10]) as

$$-\frac{1}{\beta}\frac{\mathrm{d}\ln\rho_\alpha(x)}{\mathrm{d}x} = \frac{\mathrm{d}(e_\alpha\Phi(x))}{\mathrm{d}x}$$

$$+\frac{\mathrm{d}(e_\alpha^2 V_{\mathrm{self}}(x))}{\mathrm{d}x} + e_\alpha\int\mathrm{d}\mathbf{r}'\left(\sum_\gamma e_\gamma\rho_\gamma(x')h(e_\alpha,\mathbf{r};e_\gamma,\mathbf{r}')\right)\frac{\partial v(\mathbf{r}',\mathbf{r})}{\partial x},$$

$$(19)$$

where $\Phi(x)$ is the electrostatic potential created by the charge density profile $\sum_\alpha e_\alpha\rho_\alpha(x)$. By virtue of (3), the second line in (19) involves the bulk forces between, on one hand, a charge e_α, and, on the other hand, its image, the charges in the screening cloud inside the electrolyte and their images inside the wall.

In the high-dilution limit (11), the exact solution for $\rho_\alpha(x)$ is the same as if $h(e_\alpha,\mathbf{r};e_\gamma,\mathbf{r}')$ were replaced in (19) by

$$h^{(0)}(e_\alpha,\mathbf{r};e_\gamma,\mathbf{r}') = -\beta e_\alpha e_\gamma\phi^{(0)}(\mathbf{r},\mathbf{r}'),\tag{20}$$

where $\phi^{(0)}$ is the solution of the inhomogeneous Debye equation (15) with $\kappa(x)$ replaced by the step function $\kappa^{(0)}(x)$ in which the density profiles, which vanish for $x < b$, are replaced by their bulk value at all distances $x > b$ from the wall. Then the second line in (19) is replaced by $\mathrm{d}[e_\alpha^2 V_{\mathrm{self}}^{\mathrm{sc}}(x)]/\mathrm{d}x$, where the screened self-interaction is equal to

$$V_{\mathrm{self}}^{\mathrm{sc}}(x) \equiv \frac{1}{2}[\phi^{(0)} - \phi_{\mathrm{D}}](\mathbf{r},\mathbf{r}')|_{\mathbf{r}=\mathbf{r}'},\tag{21}$$

while $\Phi(x)$ in the first line of (19) becomes

$$\Phi(x) = \int_b^{+\infty}\mathrm{d}x'\int\mathrm{d}\mathbf{y}\,\phi^{(0)}(x,x',\mathbf{y})\sum_\gamma e_\gamma\rho_\gamma^{\mathrm{B}}\exp[-\beta e_\gamma^2 V_{\mathrm{self}}^{\mathrm{sc}}(x')]\,\big|^{(1)},$$

$$(22)$$

where $|^{(1)}$ means that the integral must be calculated at first order in ε with $\kappa_{\mathrm{D}}b$ and $\beta e^2/D_{\mathrm{s}}b$ fixed, in the scaling regime (11).

If the electrolyte is charge-symmetric, $\Phi(x)$ vanishes, as it should be, since the system is completely symmetric. (All charge species have the same approach distance to the wall and the radii of their excluded-volume sphere do not arise at this order.) If the electrolyte is charge-asymmetric, then there appears a charge density profile originating from the differences in the self-energies, and this profile creates the electrostatic potential drop $\Phi(x)$ through the screened interaction $\phi^{(0)}$.

In the screened self-energy $V_{\mathrm{self}}^{\mathrm{sc}}(x)$, the screening of the bare self-image interaction is produced both from the charges in the screening cloud inside the electrolyte and from their images inside the wall. The screened self-interaction (21) can be split into two contributions, one which diverges as x goes to zero and another one that is regular,

$$V_{\text{self}}^{\text{sc}}(x) = V_{\text{im}}^{\text{B sc}}(x) + \frac{\kappa_{\text{D}}}{2D_{\text{S}}} \bar{L}(\kappa_{\text{D}}x; \kappa_{\text{D}}b, \Delta_{\text{el}}). \tag{23}$$

The bulk-screened self-image interaction $V_{\text{self}}^{\text{sc}}(x)$ is what the screened self-energy would be if screening were the same as in the bulk,

$$V_{\text{im}}^{\text{B sc}}(x) \equiv -\frac{\Delta_{\text{el}}}{2D_{\text{S}}} \frac{\mathrm{e}^{-2\kappa_{\text{D}}x}}{2x}. \tag{24}$$

Both $\bar{L}$ and Φ are regular functions, so that exponentials where they are arguments may be linearized, with the final result,

$$\rho_\alpha(x) = \rho_\alpha^{\text{B}}\theta(x - b) \exp\left[+\Delta_{\text{el}}\frac{\beta e_\alpha^2}{2D_{\text{S}}} \frac{\mathrm{e}^{-2\kappa_{\text{D}}x}}{2x}\right]$$
$$\times \left\{1 - \frac{\beta e_\alpha^2}{2D_{\text{S}}}\kappa_{\text{D}}\bar{L}(\kappa_{\text{D}}x; \kappa_{\text{D}}b, \Delta_{\text{el}}) - \beta e_\alpha\Phi(x) + \mathcal{O}(\varepsilon^2)\right\}, \tag{25}$$

where θ is the Heaviside function ($\theta(u) = 0$ if $u < 0$, and $\theta(u) = 1$ if $u > 0$), and $\mathcal{O}(\varepsilon^2)$ has the same meaning as in (12). The expression (25) involves three kinds of contributions: the bare self-image interaction with a bulk Debye-screening exponential factor, $V_{\text{im}}^{\text{B sc}}(x)$, which has the same expression as in the Onsager–Samaras heuristic expression, except that here $\Delta_{\text{el}} \neq -1$; the other part of the screened self-energy, which involves $\bar{L}$ and describes the discrepancy with the bulk perfect spherical screening, arising from combined steric and polarization effects, as discussed in the next section; the electrostatic potential drop $\Phi(x)$.

In regimes (1) and (2), $\kappa_{\text{D}}b \ll 1$ (see (17) and (18)). The explicit expressions of $\bar{L}$ is [5],

$$\bar{L}(\kappa_{\text{D}}x; \kappa_{\text{D}}b, \Delta_{\text{el}}) = (1 - \Delta_{\text{el}}^2) \int_1^\infty \mathrm{d}t\, \frac{\mathrm{e}^{-2t\kappa_{\text{D}}x}}{\left(t + \sqrt{t^2 - 1}\right)^2 - \Delta_{\text{el}}} + O(\kappa_{\text{D}}b). \tag{26}$$

It is valid for $-1 \leq \Delta_{\text{el}} \leq 1$ [15]. $\bar{L}$ decays exponentially over the length scale $\xi_{\text{D}}/2$ at large distances from the wall. The expression of $\Phi(x)$ in the case $\Delta_{\text{el}} < 1$ has been given in ref. [5] and rewritten in ref. [13]. In regime (1), $\beta e^2/(2D_{\text{s}}b)$ is fixed, and $\beta e_\alpha\Phi(x)$ is proportional to ε times a linear combination of functions of $\kappa_{\text{D}}x$, where one coefficient involves $\ln(\kappa_{\text{D}}b)$ plus a function of $\beta e^2/(2D_{\text{s}}b)$ (which tends to a constant in regime (2) where $\beta e^2/(2D_{\text{s}}b)$ vanishes). If $\Delta_{\text{el}} \leq 0$, we can take the limit $\kappa_{\text{D}}b = 0$ (so that $\Delta_{\text{el}}\beta e^2/(2D_{\text{s}}b)$ goes to $-\infty$), and then $\Phi(x)$ becomes independent of b. Moreover, $\Phi(x)$ has been calculated for $\Delta_{\text{el}} = 1$ in ref. [15]. In the latter case, $\beta e_\alpha\Phi(x)$ at order ε proves to be independent of b.

The density profiles result from the competition between several effects:

  – The polarization effects due to the difference between the dielectric constants, which are attractive or repulsive according to the sign of $D_{\text{w}} - D_{\text{s}}$.
  – The steric deformation of screening clouds created by the impenetrability of the wall. If $D_{\text{w}} = D_{\text{s}}$, $\bar{L}$ contains no other effect and is positive at all distances: the geometric repulsion from the impenetrable wall hinders the stabilizing effect of Coulomb interactions.

– The interaction between each charge and the electrostatic potential drop created by the charge density profile that arises from the differences between the full screened self-energies when the electrolyte is charge-asymmetric.

5. Steric deformation of screening clouds and polarization effects

5.1 *Exact effective pair interaction along the wall*

The effective pair interaction $w_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')$ is defined by the relation $h(e_\alpha, \mathbf{r}; e_\gamma, \mathbf{r}') = \exp[-\beta w_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')] - 1$. In the bulk there is 'perfect screening': at relative distances larger than the microscopic characteristic lengths, the effective pair interaction between two charges in the electrolyte decays exponentially, and this is linked to a spherical symmetry of the set formed by a charge and its screening cloud [10].

In the generic case where both D_{s} and D_{w} are finite ($\Delta_{\mathrm{el}} \neq \pm 1$), $w_{\alpha\gamma}(x, x', \mathbf{y})$ decays as $1/y^3$ at large relative distances y along the wall, which corresponds to a breakdown of the spherical symmetry of the set formed by a charge, its screening cloud, and their images inside the wall. In other words, the deformation of a screening cloud inside the electrolyte created by the impenetrability of the wall (steric effect) is not compensated by the imperfect polarization of the dielectric wall described by the image and the image screening cloud inside the wall, so that the 'perfect' exponential screening in the bulk rotationally-invariant situation is destroyed.

If all species have the same closest approach distance to the wall, it can be shown that the coefficient of the $1/y^3$ tail is factorized into two effective dipoles $D_\alpha(x)$ and $D_\gamma(x')$ [16]

$$h(e_\alpha, \mathbf{r}; e_\gamma, \mathbf{r}') \underset{y \to \infty}{\sim} -\beta \frac{D_\alpha(x) D_\gamma(x')}{D_{\mathrm{s}} y^3}. \tag{27}$$

In the dilute regime, $D_\alpha(x)$ decays exponentially over the same screening length as in the bulk [13]. At distances from the wall larger than a few screening lengths, $D_\alpha(x)$ takes the same functional form as the high-dilution limit $D_\alpha^{(0)}(x)$, where

$$D_\alpha^{(0)}(x) = -e_\alpha \sqrt{\frac{2D_{\mathrm{w}}}{D_{\mathrm{s}}}} \frac{\mathrm{e}^{-\kappa_{\mathrm{D}}(x-b)}}{\kappa_{\mathrm{D}}}. \tag{28}$$

In dilute solutions, many-body effects reduce to the introduction of effective charges $Z_\alpha^{\mathrm{w\,eff}}$ and of a screening length κ^{-1} in place of the bare solvated charge Z_α and the Debye length κ_{D}^{-1}. At relative order ε [13], they involve both screened interactions via one or two intermediate charges in $w_{\alpha\alpha'}$, and the three effects which are exhibited in the density profile (25) and which modify the expression of ϕ at first order in ε.

In the special cases $D_{\mathrm{s}}/D_{\mathrm{w}} = 0$ or $D_{\mathrm{s}}/D_{\mathrm{w}} = +\infty$ ($\Delta_{\mathrm{el}} = \pm 1$), the wall is an ideal conductor or an ideal 'anticonductor', respectively. If $\Delta_{\mathrm{el}} = 1$, the set made by a charge, its screening cloud inside the electrolyte, and their images have spherical symmetry, and the exponential screening of the bulk is restored in $w_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')$ at large distances in all directions. If $\Delta_{\mathrm{el}} = -1$, $w_{\alpha\gamma}(\mathbf{r}, \mathbf{r}')$ also falls off exponentially,

though only the even multipole moments of the considered set vanish [10]. This can be checked at leading order in the special regime (11), where $w_{\alpha\gamma}^{(0)}(\mathbf{r}, \mathbf{r}') = -\beta e_\alpha e_\gamma \phi^{(0)}(\mathbf{r}, \mathbf{r}')$: if $\Delta_{\mathrm{el}} = \pm 1$,

$$\phi^{(0)}(\mathbf{r}, \mathbf{r}') \underset{y \gg b}{\sim} \phi_{\mathrm{D}}(\mathbf{r} - \mathbf{r}') - \Delta_{\mathrm{el}} e^{2\kappa_{\mathrm{D}} b} \phi_{\mathrm{D}}(\mathbf{r}^\star - \mathbf{r}'), \tag{29}$$

where the Debye bulk screened interaction given in (9) decays exponentially.

5.2 *Screened self-energy*

In the case where $\Delta_{\mathrm{el}} = \pm 1$ and $\kappa_{\mathrm{D}} b = 0$, $V_{\mathrm{self}}^{\mathrm{sc}}(x)$ is reduced to the bulk-screened self-image interaction $V_{\mathrm{im}}^{\mathrm{B\,sc}}(x)$, as in formula (13) for $\Delta_{\mathrm{el}} = -1$. If $\Delta_{\mathrm{el}} = \pm 1$ and $\kappa_{\mathrm{D}} b = 0$,

$$\bar{L}(\kappa_{\mathrm{D}} x) = 0 \quad \text{and} \quad V_{\mathrm{self}}^{\mathrm{sc}}(x) = V_{\mathrm{im}}^{\mathrm{B\,sc}}(x). \tag{30}$$

The interpretation of (30) is that the 'perfect screening' at large distances when the wall is ideally conductive ($\Delta_{\mathrm{el}} = 1$) or ideally 'anticonductive' ($\Delta_{\mathrm{el}} = -1$) also arises at short distances when no steric effect prevents it ($\kappa_{\mathrm{D}} b = 0$).

Moreover, the large-x tail of the complete screened self-energy $V_{\mathrm{self}}^{\mathrm{sc}}(x)$ (21), with both steric and polarization effects, reads

$$\frac{e_\alpha^2}{D_{\mathrm{S}}} V_{\mathrm{self}}^{\mathrm{sc}}(x) \underset{x \to +\infty}{\sim} \frac{e_\alpha^2}{D_{\mathrm{S}}} \frac{e^{-2\kappa_{\mathrm{D}}(x-b)}}{4x}. \tag{31}$$

It is independent of D_{W}, unlike the bare image-interaction $V_{\mathrm{self}}(x)$ which involves a multiplicative factor $-\Delta_{\mathrm{el}}$, as already noticed in ref. [17]. (In fact, it is equal to $V_{\mathrm{self}}^{\mathrm{sc}}(x; \kappa_{\mathrm{D}} b = 0, \Delta_{\mathrm{el}} = -1)$.) In other words, Coulomb screening prevents any dependence of $V_{\mathrm{self}}^{\mathrm{sc}}(x)$ upon the medium on the other side of the interface at distances larger than ξ from the wall. We point out again that this effect is purely repulsive, whatever the ratio $D_{\mathrm{W}}/D_{\mathrm{S}}$ may be, namely whether the wall is electrostatically attractive or repulsive.

6. Screening in the density profiles

6.1 *Charge symmetric electrolyte and screened self-energy*

In a symmetric $Z{:}Z$ electrolyte where the excluded-volume spheres have the same radii, by symmetry, the charge density profile is flat, $\sum_\alpha e_\alpha \rho_\alpha(x) = 0$ at any dilution and coupling strength in the fluid phase. Then, the electrostatic potential drop $\Phi(x)$ also vanishes in the absence of any external charges, by virtue of Poisson equation, $\Delta\Phi(x) = -(4\pi/D_{\mathrm{S}}) \sum_\alpha e_\alpha \rho_\alpha(x)$. As a consequence, both species $+Ze$ and $-Ze$ have the same density profile, $\rho_+^{\mathrm{sym}}(x) = \rho_-^{\mathrm{sym}}(x)$, and the latter is reduced to the Boltzmann factor of the full screened self-energy,

$$\rho_\alpha^{\mathrm{sym}}(x) = \rho_{\mathrm{self},\alpha}^{\mathrm{sc}}(x) \equiv \rho_\alpha^{\mathrm{B}} \exp\!\left[-\beta e_\alpha^2 V_{\mathrm{self}}^{\mathrm{sc}}(x)\right]. \tag{32}$$

If $\Delta_{\mathrm{el}} = 0$, $V_{\mathrm{self}}^{\mathrm{sc}}(x)$ is reduced to the contribution from $\bar{L}$, and the density profile is only determined by the steric repulsion from the wall [18]. If $\Delta_{\mathrm{el}} \neq 0$, the behavior in the very vicinity of the wall is ruled by the bare self-image interaction $V_{\mathrm{self}}(x)$. At distances x larger than $|\Delta_{\mathrm{el}}|\beta e^2/D_{\mathrm{s}}$, the repulsive effect of the (steric/polarization) deformation of screening clouds and their images dominates, even in the case of an electrostatically attractive wall, as exhibited by the universal large-distance tail (31).

6.2 *Charge asymmetric electrolyte and electrostatic potential drop*

When species have different charges, there appears a contribution in the charge-density profile from the part $\rho_{\mathrm{self},\alpha}^{\mathrm{sc}}(x)$ of the density profiles with only the contribution from the screened self-energy (see (32)). The structure of the 'double' layer of the charge density profile $\sum_{\alpha} e_{\alpha}\rho_{\alpha}(x)$ in the electrolyte depends on its composition $\{e_{\alpha}, \rho_{\alpha}^{\mathrm{B}}\}_{\alpha=1,\ldots,n_s}$. In a three-component electrolyte more charge layers can appear [5]. $\rho_{\mathrm{self},\alpha}^{\mathrm{sc}}(x)$ is significant not only up to the scale $|\Delta_{\mathrm{el}}|\beta e^2/D_{\mathrm{s}}$ of the charge-image interaction, but also up to the scale ξ_{D}, because of the steric/polarization deformation of screening clouds described by $\bar{L}$.

The electrostatic potential drop $\Phi(x)$ (22), which is created at leading order in ε by $\sum_{\alpha} e_{\alpha}\rho_{\mathrm{self},\alpha}^{\mathrm{sc}}(x)$ through the screened interaction $\phi^{(0)}$, decays only as $\Phi_{\mathrm{as}}\exp[-\kappa_{\mathrm{D}}x]$, whereas $\rho_{\mathrm{self},\alpha}^{\mathrm{sc}}(x)$ falls off exponentially over the range $1/(2\kappa_{\mathrm{D}})$. Therefore, $\Phi(x)$ dominates the large-distance behavior of each density profile $\rho_{\alpha}(x)$. Unlike the coefficient of the tail of the screened self-energy (31), the coefficient Φ_{as} (as well as $\Phi(x=b)$) depends not only on the parameters characterizing the interface, Δ_{el} and b, but also on the composition of the fluid.

At large distances from the interface, the bulk local neutrality (5) cancels the contribution from the electrostatic potential drop in the total particle density $\sum_{\alpha} \rho_{\alpha}(x)$, and the latter density behaves as $-\beta\sum_{\alpha} e_{\alpha}^2 V_{\mathrm{self}}^{\mathrm{sc}}(x)$. On the contrary, the charge density profile at large distances is controlled by the tail of the electrostatic potential,

$$\sum_{\alpha} e_{\alpha}\rho_{\alpha}(x) \underset{x \to +\infty}{\sim} -\frac{\kappa_{\mathrm{D}}^2}{4\pi}\,\Phi_{\mathrm{as}}\,\frac{\mathrm{e}^{-\kappa_{\mathrm{D}}x}}{4x}. \tag{33}$$

6.3 *Global charge and global neutrality*

The global charge carried by the fluid per unit area, $Q \equiv \int_b^{+\infty}\sum_{\alpha} e_{\alpha}\rho_{\alpha}(x)$, can be split, at leading order in ε, into two contributions: σ_{self} corresponding to $\sum_{\alpha} e_{\alpha}\rho_{\mathrm{self},\alpha}^{\mathrm{sc}}(x)$, and σ_{Φ} arising from $\rho_{\alpha}^{\mathrm{B}}[-\beta e_{\alpha}\Phi(x)]$. At leading order σ_{self} and σ_{Φ} are both proportional to $\beta\sum_{\alpha} e_{\alpha}^3\rho_{\alpha}$. If D_{w} is finite, they cancel each other in order to ensure the global neutrality $Q = 0$, which is the analog of the bulk charge neutrality (5) in the vicinity of an insulating boundary. If $D_{\mathrm{w}} = +\infty$, Q is opposite to the influence charge induced by the electrolyte inside the conductive wall at fixed potential [15].

We notice that a similar quantum effect proportional to the Planck constant $\hbar$ arises in the particle–hole gas in a semi-conductor in the vicinity of an interface.

Indeed, the wavefunctions vanish Gaussianly fast close to the wall over distances equal to the de Broglie thermal wavelengths, which are different when particles and holes have different masses [19].

6.4 *Kinetic pressure on the wall and contact theorem*

The contact theorem [20] gives the difference between the bulk thermodynamical pressure P^{B} and the kinetic pressure on the wall, $\sum_{\alpha}^{n_s} \rho_{\alpha}^{\mathrm{B}}(x = b)/\beta$. The densities at contact $\rho_{\alpha}^{\mathrm{B}}(x = b)$s involve the closest approach distance b and the wall dielectric constant D_{W}. Compensations between the kinetic pressure and various interaction contributions ensure that the bulk pressure is independent of the parameters b and D_{W}, namely from the specific forms of the interactions between particles and the wall, whether the latter interactions are purely geometric repulsions or Coulombic couplings.

7. Surface tension

By virtue of Gibbs adsorption equation, the difference between the surface tensions with or without the electrolyte is related to the excess particle density of the electrolyte,

$$\Delta\gamma = -\int_0^1 \mathrm{d}\lambda \int_b^{+\infty} \mathrm{d}x \sum_{\alpha=1}^{n_s} [\rho_{\alpha}(x;\lambda) - \rho_{\alpha}^{\mathrm{B}}(\lambda)] \frac{\mathrm{d}\mu_{\alpha}}{\mathrm{d}\lambda}, \tag{34}$$

where $\rho_{\alpha}^{\mathrm{B}}(\lambda = 0) = 0$, $\rho_{\alpha}^{\mathrm{B}}(\lambda = 1) = \rho_{\alpha}^{\mathrm{B}}$ and $\sum_{\alpha} e_{\alpha} \rho_{\alpha}^{\mathrm{B}}(\lambda) = 0$ for all λs. The excess particle density $\sum_{\alpha} [\rho_{\alpha}(x) - \rho_{\alpha}^{\mathrm{B}}]$ is of order $\rho\varepsilon$ and so, in order to get $\Delta\gamma$ at leading order in ε, we have to consider $\mathrm{d}\mu_{\alpha}$ only at leading order, namely $\mathrm{d}\mu_{\alpha}^{(0)} = \mathrm{d}\rho_{\alpha}^{\mathrm{B}}/(\rho_{\alpha}^{\mathrm{B}}\beta)$. Because of the bulk neutrality (5), the potential drop $\Phi(x)$ in expression (25) of the density profiles does not contribute to the excess surface tension $\Delta\gamma$ at leading order in ε, and the latter is determined only by the part $\rho_{\mathrm{self},\alpha}^{\mathrm{sc}}(x)$ (see (32)) of the density profile.

In regimes (1) and (2), both ε and $\kappa_{\mathrm{D}}b$ are small. In a double expansion in ε and $\kappa_{\mathrm{D}}b$ with $\beta e^2/D_{\mathrm{s}}b \propto \varepsilon/(\kappa_{\mathrm{D}}b)$ kept fixed, we get that $\beta\Delta\gamma = \beta\Delta\gamma^{(0)} + \kappa_{\mathrm{D}}^2 \mathcal{O}(\varepsilon, \kappa_{\mathrm{D}}b)$, where $\mathcal{O}(\varepsilon, \kappa_{\mathrm{D}}b)$ denotes terms that are either of order ε or of order $\kappa_{\mathrm{D}}b$, and

$$\beta\Delta\gamma^{(0)}(\varepsilon, \kappa_{\mathrm{D}}b) = \frac{\kappa_{\mathrm{D}}^2}{16\pi} \left[B_{\mathrm{im}}\left(\varepsilon, \kappa_{\mathrm{D}}b; \Delta_{\mathrm{el}}\right) + B_{\bar{L}}(\Delta_{\mathrm{el}})\right]. \tag{35}$$

B_{im} is created by the bulk-screened self-image interaction in the Debye limit $V_{\mathrm{im}}^{\mathrm{B\,sc}}(x)$,

$$B_{\mathrm{im}}(\varepsilon, \kappa_{\mathrm{D}}b; \Delta_{\mathrm{el}})$$

$$= \Delta_{\mathrm{el}} \frac{4\pi}{\kappa_{\mathrm{D}}^2} \sum_{\alpha=1}^{n_s} \rho_{\alpha}^{\mathrm{B}} Z_{\alpha}^2 \frac{\beta e^2}{D_{\mathrm{S}}} \left[\ln(2\kappa_{\mathrm{D}}b) + g\left(|\Delta_{\mathrm{el}}| \frac{Z_{\alpha}^2 \beta e^2}{4D_{\mathrm{S}}b}\right) + C - \frac{1}{2}\right], \tag{36}$$

with $\beta e^2/(2D_{\mathrm{s}}b) = \varepsilon/(\kappa_{\mathrm{D}}b)$ and

$$g(u) \equiv \frac{e^u - 1}{u} - 1 - \int_0^u \mathrm{d}t \frac{e^t - 1}{t}. \tag{37}$$

$B_{\bar{L}}(\Delta_{\mathrm{el}})$, which originates from $\bar{L}(\kappa_{\mathrm{D}}x; \kappa_{\mathrm{D}}b = 0, \Delta_{\mathrm{el}})$ in the density profile, describes the deformation with respect to spherical symmetry arising from steric and polarization effects,

$$B_{\bar{L}}(\Delta_{\mathrm{el}}) = (1 - \Delta_{\mathrm{el}}) \left[\ln 2 + \frac{1 - \Delta_{\mathrm{el}}}{2\Delta_{\mathrm{el}}} \ln(1 - \Delta_{\mathrm{el}}) \right]. \tag{38}$$

We notice that $B_{\bar{L}}(\Delta_{\mathrm{el}} = \pm 1) = 0$, because $\bar{L}(\kappa_{\mathrm{D}}x; \kappa_{\mathrm{D}}b = 0, \Delta_{\mathrm{el}} = \pm 1) = 0$ (see (30)): if $\kappa_{\mathrm{D}}b = 0$ the compensation of the steric deformation of screening clouds by the polarization inside the ideal conductor/'anticonductor' wall ($\Delta_{\mathrm{el}} = \pm 1$) operates at all distances (not only at large distances y).

In regime (2) (see (18)), $\beta e^2/(2D_{\mathrm{s}}b)$ tends to zero, because $(\beta e^2/2D_{\mathrm{s}}) \ll b \ll \xi_{\mathrm{D}}$ whatever the sign of Δ_{el} is. In this regime, ε vanishes faster than $\kappa_{\mathrm{D}}b$, and $\beta e^2/(2D_{\mathrm{s}}b) \propto \varepsilon/(\kappa_{\mathrm{D}}b)$ must tend to zero at fixed $\kappa_{\mathrm{D}}b$ in (36). As a result, $\Delta\gamma^{(0)}$ is some kind of limit law where the closest approach distance b appears only through the parameter $\kappa_{\mathrm{D}}b$,

$$\beta\Delta\gamma^{(0)}(\varepsilon = 0, \kappa_{\mathrm{D}}b) = \frac{\kappa_{\mathrm{D}}^2}{16\pi} \left[\Delta_{\mathrm{el}} \left(\ln(2\kappa_{\mathrm{D}}b) + C - \frac{1}{2} \right) + B_{\bar{L}}(\Delta_{\mathrm{el}}) \right]. \tag{39}$$

In regime (1) (see (17)), $\beta e^2/(2D_{\mathrm{s}}b)$ is finite. For an electrostatically attractive wall ($\Delta_{\mathrm{el}} > 0$), we cannot consider the limit $b \ll (\beta e^2/2D_{\mathrm{s}}) \ll \xi_{\mathrm{D}}$, where $\Delta_{\mathrm{el}}\beta e^2/(2D_{\mathrm{s}}b)$ tends to $+\infty$: there is an irreducible dependence on b. On the contrary, for an electrostatically repulsive wall ($\Delta_{\mathrm{el}} < 0$), we can take the previous limit, where $\Delta_{\mathrm{el}}\beta e^2/(D_{\mathrm{s}}b)$ goes to $-\infty$. In this limit, $\kappa_{\mathrm{D}}b$ vanishes faster than ε, and we must set $\kappa_{\mathrm{D}}b = 0$ at fixed ε in (36). We get that, if $\Delta_{\mathrm{el}} \leq 0$,

$$\beta\Delta\gamma^{(0)}(\varepsilon, \kappa_{\mathrm{D}}b = 0) = \frac{\kappa_{\mathrm{D}}^2}{16\pi} \left\{ -|\Delta_{\mathrm{el}}| \left[\ln \left(|\Delta_{\mathrm{el}}| \frac{\beta e^2 \kappa_{\mathrm{D}}}{2D_{\mathrm{s}}} \right) + 2C - \frac{3}{2} \right] \right.$$

$$\left. - |\Delta_{\mathrm{el}}| \frac{\sum_\alpha \rho_\alpha^{\mathrm{B}} Z_\alpha^2 \ln Z_\alpha^2}{\sum_\gamma \rho_\gamma^{\mathrm{B}} Z_\gamma^2} + B_{\bar{L}}(\Delta_{\mathrm{el}}) \right\}. \tag{40}$$

In the case of a 1:1 electrolyte, the valence term with $Z_\alpha^2 \ln Z_\alpha^2$ vanishes, and (40) yields the expression derived by Dean and Horgan [21].

Equation (40) is a universal law independent of the closest approach distance to the wall, but which still involves the parameter Δ_{el}, because the density profiles at all distances from the wall contribute to $\Delta\gamma^{(0)}$. When $\Delta_{\mathrm{el}} = -1$ and $\kappa_{\mathrm{D}}b = 0$, the density profile is reduced to the contribution from $e_\alpha^2 V_{\mathrm{im}}^{\mathrm{B\,sc}}(x)$, which happens to coincide with the large-distance (31) tail of $V_{\mathrm{self}}^{\mathrm{sc}}(x)$. This is the reason why the Onsager and Samaras formula (14) is retrieved for a $Z:Z$ electrolyte, when Δ_{el} is set to -1 in (40).

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8. Conclusion

As a conclusion we stress that the exact analytical density profiles have been obtained at any distance x from the interface. Therefore, they enable us to get the exact expression for the surface tension, which is an extension of Onsager and Samaras formula to other situations:

- an electrolyte with a charge asymmetry, which results into the creation of a charge double layer and a corresponding electrostatic potential drop $\Phi(x)$,
- a finite value of the ratio between the wall dielectric constant D_w and that of the solvent, D_s, so that polarization does not compensate the steric deformation of screening clouds near the interface and there is only dipolar screening along the wall,
- a ratio $D_\mathrm{w}/D_\mathrm{s}$ bigger than one, and even the limit $D_\mathrm{w}/D_\mathrm{s} = +\infty$, where the insulating medium is replaced by an ideal conductor. Then, the range b of the short-distance repulsion from the wall, which prevents the collapse of all charges onto the electrostatically attractive wall, irreducibly arises in the structure of the leading correction in density to the ideal-solution surface tension.

The same diagrammatic techniques enable one to calculate the density profiles in an electrolyte between two plates separated by a finite distance, and which may be either insulating or ideally conductive, with a possible external surface charge. Therefore, several other screening effects can be studied in this confined geometry; for instance, the screening in an electrolyte between two metallic electrodes. The limit law for the surface tension, as well as the force between the two plates separated by the electrolyte, could be derived for generic values of the ratios between the dielectric constants of the two plates and that of the solvent.

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