Asymptotic analysis of the Poisson–Boltzmann equation describing electrokinetics in porous media

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Abstract
We consider the Poisson–Boltzmann equation in a periodic cell, representative of a porous medium. It is a model for the electrostatic distribution of N chemical species diluted in a liquid at rest, occupying the pore space with charged solid boundaries. We study the asymptotic behaviour of its solution depending on a parameter β, which is the square of the ratio between a characteristic pore length and the Debye length. For small β we identify the limit problem which is still a nonlinear Poisson equation involving only one species with maximal valence, opposite to the average of the given surface charge density. This result justifies the *Donnan effect*, observing that the ions for which the charge is that of the solid phase are expelled from the pores. For large β we prove that the solution behaves like a boundary layer near the pore walls and is constant far away in the bulk. Our analysis is valid for Neumann boundary conditions (namely for imposed surface charge densities) and establishes rigorously that solid interfaces are uncoupled from the bulk fluid so that simplified additive theories, such as the popular Derjaguin, Landau, Verwey and Overbeek approach, can be used. We show that the asymptotic behaviour is completely different in the case of Dirichlet boundary conditions (namely for imposed surface potential).

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1. Introduction

Originally proposed at the dawn of the 20th century by Gouy and Chapman [10, 5], the Poisson–Boltzmann (PB) equation is still the corner-stone of most of the theoretical descriptions of electrokinetic phenomena. However, many works in the past few decades have emphasized the limitations of such a model. The ions are only represented by their charge, they do not have any volume and the correlations are neglected. The molecular nature of the solvent and further specific forces (such as the London dispersion) are completely ignored [4, 11]. Thus the domain of validity appears to be relatively narrow, typically in the regime of dilute simple (most of the time monovalent) electrolytes. Nevertheless, because of its simplicity, most of the theories of equilibrium and transport in charged diphasic media are still direct generalizations of the PB approach. For example, geological media (such as clays) [17, 22], electrochemistry [3, 12] and colloidal physics [15] are still based on the original concepts described by the PB equation.

The success of such an approach is due to several reasons. It justifies the popular Derjaguin, Landau, Verwey and Overbeek (DLVO) theory [24] that explains the stability of charged suspensions. In the case of charged porous media, the PB approach is also particularly significant because it yields the equilibrium electrostatic properties of the materials and it can be easily coupled to further equations in order to provide a global model of the system. Indeed, for transport properties, the PB equation can be extended in order to give the Poisson–Nernst–Planck (PNP) formalism which describes non-equilibrium processes in complex systems [26]. For example, in the case of clays, the description of electrokinetic processes in the large pores (meso- and macroporosities) can be performed thanks to the PB equation [19]. The molecular nature of the system is found to be important only for micropores (typically for distances less than 2 nm) [16].

In porous media, the PB model exhibits two different regimes, depending on the values of the salt concentration and of the pore size.

- If the pore size L is much larger than the Debye length λ_D of the electrolyte, the solid charge is screened by the microscopic ions. Thus, the local charge density is globally zero, away from the interface. Because of the relatively small value λ_D, this case corresponds to numerous applications. The solid interfaces are uncoupled so that the DLVO approach is valid. Far away from the interface, the Coulombic forces can be modelled by effective parameters, such as the effective charge [23] or the zeta potential.
- Conversely, if the pore size L is much smaller than λ_D, the charge of the solid surface is not screened. It means that the resulting electrostatic force is important anywhere in the material. Ions for which the charge is the same as that of the solid phase are expelled from the material (Donnan effect) [11]. The electro-osmotic flux becomes especially important. This case is significant because it corresponds to nanoporosities at low salt concentration.

The two asymptotic limits can be taken into account thanks to the coupling parameter $\beta = (L/\lambda_D)^2$. The large pore size domain (large β) corresponds to most of the porous systems. Nevertheless, many porous materials exhibit microscopic pores for which the opposite limit (small β) is relevant. For example, montmorillonite clays have different porosities, and the smallest ones, which are obtained at very low hydration, are even of the order of molecular distances.

The goal of the present paper is to give a rigorous mathematical analysis of these two opposite asymptotic limits. The paper is organized as follows. Section 2 introduces the model and defines the relevant reduced units. Section 3 describes precisely the geometry of the porous cell and discusses the issue of the existence and uniqueness of the solution to the PB equation.

Section 4 studies the limit case of very small pores, i.e. when β goes to zero. Section 5 is concerned with the opposite situation of very large pores, when β goes to infinity. Finally, section 6 investigates the case of Dirichlet boundary conditions (namely for imposed surface potential) instead of Neumann boundary conditions (namely imposed surface charge). A brief description of our main results is given in the following section after introducing the necessary notations.

2. The model and our main results

We consider the PB system which describes the electrostatic distribution of N chemical species diluted in a liquid at rest, occupying a porous medium with charged solid boundaries. The electrostatic potential Ψ^* is calculated from the Poisson equation

$$\mathcal{E} \Delta \Psi^* = -e \sum_{j=1}^{N} z_j n_j^* \qquad \text{in the bulk,} \tag{1}$$

where $\mathcal{E} = \mathcal{E}_0 \mathcal{E}_r$ is the dielectric constant of the solvent, e is the electron charge and n_j^*, $1 \leqslant j \leqslant N$, are the species concentrations. Since the pore walls are charged, the corresponding boundary condition is of Neumann type

$$\mathcal{E} \nabla \Psi^* \cdot \boldsymbol{n} = -\sigma^* \qquad \text{on the surface,} \tag{2}$$

where σ^* is a given surface charge and $\boldsymbol{n}$ is the unit exterior normal. Following the literature we include a minus sign in (2) which means that σ^* is positive for a negatively charged surface.

At equilibrium the species concentrations n_j^* are given by the Boltzmann distribution which corresponds to a balance between the chemical potential and the electrical field

$$\nabla(k_B T \ln n_j^*) = -\nabla(z_j e \Psi^*). \tag{3}$$

where z_j is the valence of the jth species, k_{B} the Boltzmann constant and T the temperature. It follows from (3) that there exist positive constants $n_j^*(\infty)$ (called infinite dilution concentrations) such that

$$n_j^* = n_j^*(\infty) \exp\left\{ -\frac{z_j e \Psi^*}{k_{\mathrm{B}} T} \right\}. \tag{4}$$

The PB system is the combination of (1) and (4), together with the boundary condition (2).

In order to make an asymptotic analysis of the PB system, we first adimensionalize equations (1), (2), (4). We denote by L the characteristic pore size and by n_{c} the characteristic concentration. We introduce the Debye length defined by

$$\lambda_{\mathrm{D}} = \sqrt{\frac{\mathcal{E} k_{\mathrm{B}} T}{e^2 n_{\mathrm{c}}}},$$

and define a parameter

$$\beta = \left(\frac{L}{\lambda_{\mathrm{D}}} \right)^2. \tag{5}$$

The parameter β is the fundamental physical characteristic which drives the transport properties of an electrolyte solution in a porous media. For large β the electrical potential is concentrated in a diffuse layer next to the liquid/solid interface. Co-ions, for which the charge is the same as that of the solid phase are able to go everywhere in the pores because the repelling electrostatic force of the solid phase is screened by the counterions. The electrostatic phenomena are mainly surfacic, and the interfaces are globally independent. For small β, co-ions do not have access

to the very small pores (Donnan effect). The local electroneutrality condition is not valid anymore and the electric fields of the solid interfaces are coupled.

Furthermore, we define a characteristic surface charge density σ_c by

$$\sigma_c = \frac{\mathcal{E} k_B T}{eL},$$

and adimensionalized quantities

$$\sigma = \frac{\sigma^*}{\sigma_c}, \qquad \Psi = \frac{e\Psi^*}{k_B T}, \qquad n_j = \frac{n_j^*}{n_c}, \qquad n_j^0(\infty) = \frac{n_j^*(\infty)}{n_c}.$$

Rescaling the space variable $y = x/L$ yields the adimensionalized PB system

$$\Delta_y \Psi = -\beta \sum_{j=1}^{N} z_j n_j(\Psi) \qquad \text{with } n_j(\Psi) = n_j^0(\infty) e^{-z_j \Psi} \text{ in the bulk,} \tag{6}$$

and

$$\nabla_y \Psi \cdot \boldsymbol{n} = -\sigma \qquad \text{on the surface.} \tag{7}$$

The goal of the present paper is to study the limit of equations (6) and (7) when the parameter β is either very small or very large. Section 3.2 gives a precise mathematical framework for the PB system. To discuss our results we sort the valences by increasing order and we assume that there are both anions and cations

$$z_1 < z_2 < \cdots < z_N \qquad \text{and} \qquad z_1 < 0 < z_N.$$

Section 4 is devoted to the asymptotic analysis of (6)–(7) when β goes to zero. This case corresponds to very small pores, $L \ll \lambda_D$. In view of the definition of the Debye length λ_D, a small value of β corresponds also to a small characteristic concentration n_c. The asymptotic regime depends on the sign of the averaged charge $\int_S \sigma \, dS$. If it is negative (which means that the surface is positively charged), then theorem 11 states that only the anion with the most negative valence (z_1) is important and that the potential behaves as

$$\Psi \approx \frac{\log \beta}{z_1} + \varphi_0,$$

where φ_0 is the solution of the reduced system, involving only the species 1,

$$\begin{cases} \Delta \varphi_0 = -z_1 n_1^0(\infty) e^{-z_1 \varphi_0} & \text{in the bulk,} \\ \nabla \varphi_0 \cdot \boldsymbol{n} = -\sigma & \text{on the surface.} \end{cases}$$

Note that the constant $\log \beta / z_1$ is going to $+\infty$ since $z_1 < 0$: it is a manifestation of the singularly perturbed character of the asymptotic analysis. As a consequence, the cation concentrations go to zero while the ion concentrations blow up as $n_j = O(\beta^{-z_j/z_1})$ and $n_1 \gg n_j$ for $j \neq 1$. Of course, a symmetric behaviour (involving only the species with most positive valence z_N) holds true when the averaged charge is positive. On the other hand, when the averaged charge is zero, then the limit problem is much simpler (there is no singular perturbation) and is given by theorem 14. Our analysis is reminiscent of another asymptotic limit studied in [8, 20] where the solid surface is a small sphere, the radius of which is going to zero.

Section 5 is concerned with the opposite situation when β goes to infinity. This case corresponds to very large pores, $L \gg \lambda_D$ or to large values of the characteristic concentration n_c. Such a situation is well understood in the physical and mathematical literature: it gives rise to a boundary layer (the so-called Debye's layer) close to the surface. For example, it has been analysed in [2, 18] but the analysis is restricted to 1D or similar simplified geometry. Our main

contribution, theorem 21, derives this boundary layer in a general geometric setting and gives a rigorous error estimate. To simplify the following formulas we choose the characteristic concentration $n_c = \sum_{k=1}^{N} z_k^2 n_k^*(\infty)$, which implies that $\sum_{k=1}^{N} z_k^2 n_k^0(\infty) = 1$. Locally, close to the surface, the potential behaves as

$$\Psi(y) \approx \frac{-\sigma}{\sqrt{\beta}} \exp\left\{-d(y)\sqrt{\beta}\right\},$$

where $d(y)$ is the distance between the point y and the surface. Away from the surface, the concentrations n_j are constant and satisfy the so-called bulk electroneutrality condition. Some numerical simulations for varying β can be found in our other work [1].

In the literature, one may find instead of the Neumann boundary condition (2) a Dirichlet one

$$\Psi = \zeta \qquad \text{on the surface,} \tag{8}$$

where ζ is an imposed potential. Section 6 investigates the case when the Neumann boundary condition (2) is replaced with the Dirichlet boundary condition (8). Lemma 23 gives the asymptotic behaviour for small β: the analysis is quite obvious since there are no more singular perturbations. The potential now behaves as

$$\Psi \approx \zeta + \beta \Psi_1,$$

where Ψ_1 is the solution of the corrector problem

$$\begin{cases} \Delta \Psi_1 = -\sum_{j=1}^{N} z_j n_j^0(\infty) e^{-z_j \zeta} & \text{in the bulk,} \\ \Psi_1 = 0 & \text{on the surface.} \end{cases}$$

Theorem 29 gives the asymptotic behaviour for large β. It is again a boundary layer but with a totally different profile. More precisely we establish

$$\Psi(y) \approx \Psi_{0,\zeta}\left(\sqrt{\beta}d(y)\right)$$

where $d(y)$ is the distance between the point y and the surface and $\Psi_{0,\zeta}$ is the solution of the nonlinear ordinary differential equation (114), a solution which, starting from the boundary value ζ on the surface, is exponentially decaying at infinity.

3. Geometry and existence theory for the PB equation

In this section we define the geometry and recall a classical result on the existence and uniqueness of a solution of the PB equation. Furthermore we establish L^∞-bounds for the solution.

3.1. Geometry of the porous cell

To simplify the presentation we consider a sample of a porous medium which occupies the periodic unit cell $Y = (0,1)^d$ (identified with the unit torus $\mathbb{T}^d$). The space dimension is typically $d = 2, 3$. The pore space Y_F, containing the electrolyte, is a 1-periodic smooth connected open subset of Y. More precisely, we consider a smooth partition $Y = Y_S \cup Y_F$ where Y_S is the solid part and Y_F is the fluid part. The liquid/solid interface is $S = \partial Y_S \setminus \partial Y$. It is known that for a general Y_F with a non-empty boundary S, the distance function d, defined by $d(y) = $ dist (y, S), $y \in Y_F$, is uniformly Lipschitz continuous. Let $Y_F^\mu = \{y \in Y_F : d(y) < \mu\}$. If we assume S to be smooth of class C^3, then, for sufficiently small μ, the distance function

has the same regularity, $d \in C^3(Y_F^\mu)$. Furthermore, by the collar neighbourhood theorem (see e.g. [21]), there exist tubular neighbourhoods U, $S \subset U$, isomorphic to $S \times I$, for $I \subset \mathbb{R}$, an open interval.

For $y_0 \in S$, let $\boldsymbol{n}(y_0)$ and $\boldsymbol{T}(y_0)$ denote respectively the unit normal to S at y_0 (exterior to Y_F) and the tangent hyperplane to S at y_0. Without losing generality, we can suppose that in some neighbourhood $\mathcal{N} = \mathcal{N}(y_0)$ of y_0, S is then given by $y_d = \gamma(y')$, where $y' = (y_1, \ldots, y_{d-1})$, $\gamma \in C^3(\boldsymbol{T}(y_0) \cap \mathcal{N})$ and $\nabla_{y'}\gamma(y_0') = 0$. The unit normal on S, at the point $y = (y', \gamma(y'))$ is

$$\boldsymbol{n}(y) = \frac{(\nabla_{y'}\gamma(y'), -1)}{\sqrt{1 + |\nabla_{y'}\gamma(y')|^2}}.$$

Here Y_S corresponds to $y_d > \gamma(y')$.

Following [9, p 355], for each point $y \in Y_F^\mu$, there exists a unique point $z = z(y) \in S$ such that $|y - z| = d(y)$. The points y and its closest point $z \in S$ are related by

$$y = z - \boldsymbol{n}(z)d. \tag{9}$$

By the inverse mapping theorem applied in a neighbourhood of $y_0 \in S$ (S can be covered with a finite number of such neighbourhoods), (9) defines uniquely a principal coordinate system (q', q_d) with $q' = z'$ and $q_d = d(y)$ which are C^2 functions of y. The first coordinates q' are the tangential coordinates to S while the last coordinate q_d is the signed distance to S taken with the sign $+$ in the interior of Y_F and with $-$ in its exterior. We denote by $q_d = 0$ the local representation of the boundary S in the neighbourhood of y_0. Of course, the distance function $d \in C^3$ satisfies $\nabla d(y) = -\boldsymbol{n}(q'(y))$ and $|\nabla d(y)| = 1$. Furthermore, the tangential coordinates $q' = (q_1, \ldots, q_{d-1})$ can be chosen in such a way that the Hessian matrix $[D^2\gamma(q'(y_0))]$ is diagonal at y_0. For more details we refer the reader to [9, pp 354–56].

3.2. Mathematical framework for the PB equation

We start from the adimensionalized PB system (6) and (7) (where we drop the index y for the spatial derivatives) that we complement with periodic boundary conditions on the outer boundary of the unit cell Y. More precisely, the potential Ψ is a solution of the PB equation

$$\begin{cases} -\Delta\Psi + \beta\Phi(\Psi) = 0 & \text{in } Y_F, \\ \nabla\Psi \cdot \boldsymbol{n} = -\sigma & \text{on } S, \\ \Psi \text{ is } 1 - \text{periodic}, \end{cases} \tag{10}$$

where $\sigma(y)$ is the adimensionalized charge distribution on the pore surface, $\beta > 0$ is a parameter defined by (5) as the square of the ratio of the pore size and the Debye length, and $\Phi(\Psi)$ is the bulk density of charges, a nonlinear function defined by

$$\Phi(\Psi) = -\sum_{j=1}^{N} z_j n_j(\Psi) \tag{11}$$

where n_j is the concentration of species j given, at equilibrium, as a function of the potential

$$n_j(\Psi) = n_j^0(\infty)e^{-z_j\Psi} \tag{12}$$

with a constant $n_j^0(\infty) > 0$. We assume that all valencies z_j are different. If not, we lump together different ions with the same valence. Of course, for physical reasons, all valencies z_j are integers. We rank them by increasing order,

$$z_1 < z_2 < \cdots < z_N,$$

and we denote by j^+ and j^- the sets of positive and negative valences. We also assume that there are both anions and cations, namely positive and negative valences, i.e.,

$$z_1 < 0 < z_N. \tag{13}$$

The function Φ is monotone since it is the derivative of a convex function

$$\Phi(\Psi) = \mathcal{C}'(\Psi) \qquad \text{with} \qquad \mathcal{C}(\Psi) = \sum_{j=1}^{N} n_j^0(\infty) \mathrm{e}^{-z_j \Psi}. \tag{14}$$

The boundary value problem (10) is equivalent to the following minimization problem:

$$\inf_{\varphi \in H_\#^1(Y_F)} \left\{ J(\varphi) = \frac{1}{2} \int_{Y_F} |\nabla \varphi|^2 \, \mathrm{d}y + \beta \int_{Y_F} \mathcal{C}(\phi) \, \mathrm{d}y + \int_S \sigma \varphi \, \mathrm{d}S \right\}, \tag{15}$$

with $H_\#^1(Y_F) = \{\varphi \in H^1(Y_F), \ \varphi \text{ is } 1 - \text{periodic}\}$. Note that the functional J may take infinite values for some functions $\varphi \in H_\#^1(Y_F)$ since $H_\#^1(Y_F)$ is not embedded in $L_\#^\infty(Y_F)$, except in space dimension $d = 1$. The functional J is strictly convex, which gives the uniqueness of the minimizer. Nevertheless, for arbitrary nonnegative β, n_j^c, J may be not coercive on $H_\#^1(Y_F)$ if all z_j have the same sign. Therefore, we must put a condition on the z_j so that the minimization problem (15) admits a solution. Following the literature, we impose the bulk electroneutrality condition

$$-\Phi(0) = \sum_{j=1}^{N} z_j n_j^0(\infty) = 0, \tag{16}$$

which guarantees that for $\sigma = 0$, the unique solution of (10) is $\Psi = 0$. Under assumption (16) it is easy to see that J is coercive on $H_\#^1(Y_F)$.

Remark 1. The bulk electroneutrality condition (16) is not a restriction. Actually all our results hold under the weaker assumption (13) that all valences z_j do not have the same sign. Indeed, if (16) is not satisfied, we can make a change of variables in the PB equation (10), defining a new potential $\tilde{\Psi} = \Psi + \Psi^0$ where Ψ^0 is a constant reference potential. Since the function $\Phi(\Psi^0)$ is continuous and admits the following limits at infinity

$$\lim_{\Psi^0 \to \pm\infty} \Phi(\Psi^0) = \pm\infty,$$

there exists at least one value Ψ^0 such that $\Phi(\Psi^0) = 0$. This change of variables for the potential leaves (10) invariant if we change the constants $n_j^0(\infty)$ in new constants $\tilde{n}_j^0(\infty) = n_j^0(\infty) \mathrm{e}^{-z_j \Psi^0}$. These new constants satisfy the bulk electroneutrality condition (16).

In the following we assume that the charge density is a continuous periodic function

$$\sigma(y) \in C_\#(S). \tag{17}$$

The well-posedness of the boundary value problem (10) is a classic result.

Lemma 2 ([14]). *Assume (17) and that the electroneutrality condition (16) holds true. Then problem (10), or equivalently (15), has a unique solution $\Psi \in H_\#^1(Y_F)$ such that*

$$\sum_{j=1}^{N} z_j \mathrm{e}^{-z_j \Psi} \qquad \text{and} \qquad \Psi \sum_{j=1}^{N} z_j \mathrm{e}^{-z_j \Psi}$$

are absolutely integrable.

In truth, the paper [14] proves the existence and uniqueness of a solution of the boundary value problem (10) and not of the minimization problem (15) (the method of proof relies on monotone operators and a truncation argument). However, it is not difficult to check the equivalence between (10) and (15), as already exploited in many works including [6, 8]. The interest of (15), compared to (10), is that the existence and uniqueness proof is simpler, although the regularity properties of the solution come from (10).

Actually, the issue of solution boundedness was not correctly addressed in [14], where it was merely proved that $\Psi \in L^p(Y_F)$ for every finite p. By using elementary comparison arguments we will prove a L^∞-estimate in proposition 3 (a similar result is also proved in [7]). To this end we introduce the following auxiliary Neumann problem

$$\begin{cases} -\Delta U = \dfrac{1}{|Y_F|} \displaystyle\int_S \sigma \, dS & \text{in } Y_F, \\[2mm] \nabla U \cdot \boldsymbol{n} = -\sigma & \text{on } S, \\[2mm] U \text{ is } 1 - \text{periodic}, & \displaystyle\int_{Y_F} U(y) \, dy = 0. \end{cases} \tag{18}$$

Note that (18) admits a solution $U \in H^1_\#(Y_F)$ since the bulk and surface source terms are in equilibrium. Furthermore, the zero average condition of the solution gives its uniqueness. Under condition (17) it is known that U is continuous and achieves its minimum and maximum in $\overline{Y_F}$.

Then our L^∞-bound reads as follows.

Proposition 3. *The solution Ψ of (10) satisfies the following bounds*

$$U(y) - U_m - \frac{1}{z_1} \log \max \left(1, \frac{\overline{\sigma}}{\beta z_1 n_1^0(\infty)} - \sum_{j \in j^+} \frac{z_j n_j^0(\infty)}{z_1 n_1^0(\infty)} \right) \geqslant \Psi(y) \geqslant$$

$$U(y) - U_M - \frac{1}{z_N} \log \max \left(1, \frac{\overline{\sigma}}{\beta z_N n_N^0(\infty)} - \sum_{j \in j^-} \frac{z_j n_j^0(\infty)}{z_N n_N^0(\infty)} \right), \tag{19}$$

where the symbols j^+ and j^- denote the sets of positive and negative valences, respectively, and

$$\overline{\sigma} = \frac{1}{|Y_F|} \int_S \sigma \, dS, \qquad U_m = \min_{y \in \overline{Y_F}} U(y) \quad \text{and} \quad U_M = \max_{y \in \overline{Y_F}} U(y).$$

Proof. We use the variational formulation for $\Psi - U$, which reads, for any smooth 1-periodic function φ,

$$\int_{Y_F} \nabla(\Psi - U) \cdot \nabla \varphi \, dy + \beta \int_{Y_F} \Phi(\Psi) \varphi \, dy + \overline{\sigma} \int_{Y_F} \varphi \, dy = 0. \tag{20}$$

We take $\varphi(y) = (\Psi(y) - U(y) + C)^-$, where C is a constant to be determined and, as usual, the function $f^- = \min(f, 0)$ is the negative part of f. We note that by lemma 2, $\varphi \in H^1_\#(Y_F)$ and $\Phi(\Psi)\varphi$ is integrable. It yields

$$\int_{Y_F} |\nabla \varphi|^2 \, dy + \beta \int_{Y_F} (\Phi(\Psi) - \Phi(U - C)) (\Psi - U + C)^- \, dy$$

$$+ \int_{Y_F} (\beta \Phi(U - C) + \overline{\sigma}) \varphi \, dy = 0.$$

By monotonicity of Φ the second term is nonnegative. Hence we should choose C in such a way that the coefficient in front of φ in the third term is nonpositive. If $C \geqslant U_M$, we have

$$\beta \Phi(U - C) + \overline{\sigma} \leqslant -\beta z_N n_N^0(\infty) e^{z_N(C - U_M)} - \beta \sum_{j \in j^-} z_j n_j^0(\infty) + \overline{\sigma}.$$

Thus, if it happens that

$$-\beta \sum_{j \in j^-} z_j n_j^0(\infty) + \overline{\sigma} < \beta z_N n_N^0(\infty), \tag{21}$$

we indeed take $C = U_M$ and the corresponding term is nonpositive. If (21) is not true, then our choice is

$$C = U_M + \frac{1}{z_N} \log \left(\frac{\overline{\sigma}}{\beta z_N n_N^0(\infty)} - \sum_{j \in j^-} \frac{z_j n_j^0(\infty)}{z_N n_N^0(\infty)} \right) \geqslant U_M.$$

This choice of the constant C implies that $\varphi(y) = 0$ and it yields the lower bound in (19).

Let us switch to the upper bound. We now take $\varphi(y) = (\Psi(y) - U(y) - C)^+$, where C is another constant to be determined. We note that by lemma 2, $\varphi \in H^1_\#(Y_F)$ and $\Phi(\Psi)\varphi$ is integrable. It yields

$$\int_{Y_F} |\nabla \varphi|^2 \, \mathrm{d}y + \beta \int_{Y_F} (\Phi(\Psi) - \Phi(U + C))(\Psi - U - C)^+ \, \mathrm{d}y$$
$$+ \int_{Y_F} (\beta \Phi(U + C) + \overline{\sigma}) \varphi \, \mathrm{d}y = 0.$$

By monotonicity the second term is nonnegative. Again we should choose C in such a way that the coefficient in front of φ in the third term is nonnegative. If $C + U_m \geqslant 0$, we have

$$\beta \Phi(U(y) + C) + \overline{\sigma} \geqslant -\beta z_1 n_1^0(\infty) e^{-z_1(C + U_m)} - \beta \sum_{j \in j^+} z_j n_j^0(\infty) + \overline{\sigma}.$$

Thus, if it happens that

$$\beta \sum_{j \in j^+} z_j n_j^0(\infty) - \overline{\sigma} < -\beta z_1 n_1^0(\infty), \tag{22}$$

we take $C = -U_m$. If (22) is not true, then our choice is

$$C = -U_m - \frac{1}{z_1} \log \left(\frac{\overline{\sigma}}{\beta z_1 n_1^0(\infty)} - \sum_{j \in j^+} \frac{z_j n_j^0(\infty)}{z_1 n_1^0(\infty)} \right) \geqslant -U_m.$$

This choice of the constant C gives the upper bound in (19) and the proposition is proved. $\qquad \square$

By classical regularity theory for elliptic partial differential equations, we easily deduce from proposition 3 that the solution of the PB equation is as smooth as the data are.

Corollary 4. *Suppose $S \in C^\infty$ and $\sigma \in C^\infty_\#(S)$. Then $\Psi \in C^\infty(\bar{Y}_F)$.*

4. The limit case of small β

In this section we investigate the case of small values of β which occurs for small pore sizes. Equivalently, in the case of very dilute concentrations, we can scale all concentration coefficients $n_j^0(\infty)$ by a small parameter which acts as a multiplicative factor of β. We shall prove that the solution $\Psi = \Psi_\beta$ of the PB equation (10) (with a subscript β to indicate that we study the behaviour when $\beta \to 0^+$) is uniformly bounded up to an additive constant which may blow up.

Lemma 5. *Let* Ψ_β *be the unique solution of* (10). *There exists a constant* C, *which does not depend on* β, *such that*

$$\|\Psi_\beta - \mathcal{M}(\Psi_\beta)\|_{H^1(Y_F)} \leqslant C\|\sigma\|_{L^2(S)}, \tag{23}$$

where $\mathcal{M}$ *is the averaging operator defined by* $\mathcal{M}(g) = \frac{1}{|Y_F|} \int_{Y_F} g(y)\,\mathrm{d}y.$

Proof. We recall that the variational formulation corresponding to (10) is, for any smooth 1-periodic function φ,

$$\int_{Y_F} \nabla\Psi_\beta \cdot \nabla\varphi\,\mathrm{d}y + \beta\int_{Y_F} \Phi(\Psi_\beta)\varphi\,\mathrm{d}y + \int_S \sigma\varphi\,\mathrm{d}S = 0, \tag{24}$$

where the nonlinear function Φ is defined by (11). Taking the test function $\varphi = \Psi_\beta - \mathcal{M}(\Psi_\beta)$ in (24) we get

$$\int_{Y_F} |\nabla\Psi_\beta|^2\,\mathrm{d}y + \beta\int_{Y_F} \left(\Phi(\Psi_\beta) - \Phi(\mathcal{M}(\Psi_\beta))\right)\left(\Psi_\beta - \mathcal{M}(\Psi_\beta)\right)\,\mathrm{d}y$$
$$+ \int_S \sigma(\Psi_\beta - \mathcal{M}(\Psi_\beta))\,\mathrm{d}S = 0.$$

By monotonicity of Φ the second term is nonnegative and Poincaré inequality yields the *a priori* estimate (23). □

When $\int_S \sigma\,\mathrm{d}S \neq 0$, we expect that $\mathcal{M}(\Psi_\beta)$ blows up as β tends to zero. This is already indicated by the L^∞-bounds from proposition 3. More convincingly, choosing $\varphi = 1$ in (24) leads to

$$\beta\int_{Y_F} \Phi(\Psi_\beta)\,\mathrm{d}y = -\int_S \sigma\,\mathrm{d}S, \tag{25}$$

which shows that $\mathcal{M}(\Phi(\Psi_\beta))$ blows up, at least. Note also that, for $\beta = 0$, the corresponding boundary value problem (10) has no solution. However, in the case $\int_S \sigma\,\mathrm{d}S = 0$, Ψ_β is bounded as will be proved in section 4.3.

4.1. Formal asymptotics

We first obtain by a formal method of asymptotic expansions the boundary value problem, corresponding to the limit $\beta \to 0$. There are three possibilities.

Case 1. $\int_S \sigma < 0$. Since the Neumann boundary condition (2) or (7) involves $-\sigma$, this case corresponds to positively charged walls. Therefore, it is the most negative valence z_1 which matters. Since $\Psi_\beta - \mathcal{M}(\Psi_\beta)$ is bounded, we look for an asymptotic formula

$$\Psi_\beta(y) = a_\beta + \psi_0(y) + o(1), \tag{26}$$

with a constant $a_\beta \to +\infty$ and ψ_0 a function independent of β and of zero mean in Y_F. We will see that further terms in the asymptotic expansion come in general with fractional powers of β.

The equality (25) becomes

$$-\beta\sum_{j=1}^N z_j n_j^0(\infty)\int_{Y_F} \mathrm{e}^{-z_j(a_\beta + \psi_0(x) + o(1))}\,\mathrm{d}y = -\int_S \sigma\,\mathrm{d}S.$$

Therefore, we have

$$z_1 n_1^0(\infty)\beta e^{-z_1 a_\beta} \int_{Y_F} e^{z_1(\psi_0(y)+o(1))} \, dy$$

$$+\beta \sum_{j=2}^{N} z_j n_j^0(\infty) e^{-z_j a_\beta} \int_{Y_F} e^{-z_j(\psi_0(y)+o(1))} \, dy = \int_S \sigma \, dS, \tag{27}$$

and, since $a_\beta \to +\infty$, at the leading order (27) reads

$$z_1 n_1^0(\infty)\beta e^{-z_1 a_\beta} \int_{Y_F} e^{-z_1(\psi_0(y)+o(1))} \, dy = \int_S \sigma \, dS. \tag{28}$$

From (28) we deduce

$$a_\beta = \frac{\log \beta}{z_1} + C_0, \tag{29}$$

where C_0 is a constant which may depend on β but is bounded as a function of $\beta \to 0$. This decomposition allows us to eliminate the singular part a_β in the expansion. We thus get the following nonlinear equation for $\psi_0(y)$

$$\begin{cases} -\Delta\psi_0(y) - \int_S \sigma \, dS \dfrac{e^{-z_1\psi_0}}{\int_{Y_F} e^{-z_1\psi_0(y)} \, dy} = 0 \ \text{ in } \ Y_F, \\ \nabla\psi_0 \cdot n = -\sigma \ \text{ on } \ S, \\ \psi_0 \ \text{ is } 1-\text{periodic and } \displaystyle\int_{Y_F} \psi_0 \, dy = 0. \end{cases} \tag{30}$$

In our approximate formula for Ψ_β we have neglected terms of order $O(\beta^{1-z_2/z_1})$. In the canonical case of two opposite valencies ($N = 2$, $z_1 = -z_2$), the neglected term is of order $O(\beta^2)$.

Equation (30) does not contain β. Rather than using ψ_0, it is more practical to use $\varphi_0(y) = \psi_0(y) + C_0$. Then we have

$$\Psi_\beta(y) = \frac{\log \beta}{z_1} + \varphi_0(y) + O(\beta^{1/z^-}), \tag{31}$$

and φ_0 is the solution to the boundary value problem

$$\begin{cases} -\Delta\varphi_0(y) - z_1 n_1^0(\infty) e^{-z_1\varphi_0(y)} = 0 \ \text{ in } \ Y_F, \\ \nabla\varphi_0 \cdot n = -\sigma \ \text{ on } \ S, \\ \varphi_0 \ \text{ is } 1-\text{periodic.} \end{cases} \tag{32}$$

We note that by testing (32) by a constant and integrating, we get

$$z_1 n_1^0(\infty) \int_{Y_F} e^{-z_1\varphi_0(y)} \, dy = \int_S \sigma \, dS.$$

Consequently, φ_0 solves (30) except that it is not of mean zero. We have the following simple result.

Lemma 6. *Assume that σ is a smooth bounded function such that $\int_S \sigma \, dS < 0$. Then problem (32) has a unique solution $\varphi_0 \in H_\#^1(Y_F)$ such that*

$$e^{-z_1\varphi_0} \qquad \text{and} \qquad e^{-z_1\varphi_0}\varphi_0$$

are absolutely integrable.

Proof. The corresponding functional, to be minimized, is

$$J_0(\varphi) = \frac{1}{2} \int_{Y_F} |\nabla\varphi|^2 \, dy + n_1^0(\infty) \int_{Y_F} e^{-z_1\phi} \, dy + \int_S \sigma\varphi \, dS.$$

It is strictly convex and the condition $\int_S \sigma \, dS < 0$ insures the coercivity. The rest of the proof follows that of lemma 2. $\square$

Case 2. $\int_S \sigma > 0$. Since the Neumann boundary condition (2) or (7) involves $-\sigma$, this case corresponds to negatively charged walls. Thus, it is the largest positive valence z_N which matters. At the leading order, (25) reads

$$\beta z_N n_N^0(\infty) e^{-z_N a_\beta} \int_{Y_F} e^{-z_N(\psi_0(y)+o(1))} \, dy = \int_S \sigma \, dS. \tag{33}$$

For the same asymptotic expansion (26), equation (33) allows us to compute the singular behaviour a_β and we get the following equation for the zero-mean perturbation ψ_0, $\int_{Y_F} \psi_0 \, dy = 0$

$$\begin{cases} -\Delta\psi_0 - \int_S \sigma \, dS \dfrac{e^{-z_N\psi_0}}{\int_{Y_F} e^{-z_N\psi_0(x)} \, dy} = 0 \ \text{ in } \ Y_F, \\ \nabla\psi_0 \cdot \boldsymbol{n} = -\sigma \ \text{ on } \ S, \\ \psi_0 \ \text{ is } 1 - \text{periodic and } \int_{Y_F} \psi_0 \, dy = 0. \end{cases} \tag{34}$$

By the same reasoning as in the first case, we deduce

$$\Psi_\beta(y) = \frac{\log\beta}{z_N} + \xi_0(y) + O(\beta^{1/z_N}), \tag{35}$$

where ξ_0 is the solution of

$$\begin{cases} -\Delta\xi_0(y) - z_N n_N^0(\infty) e^{-z_N\xi_0(y)} = 0 \ \text{ in } \ Y_F, \\ \nabla\xi_0 \cdot \boldsymbol{n} = -\sigma \ \text{ on } \ S, \\ \xi_0 \ \text{ is } 1 - \text{periodic}. \end{cases} \tag{36}$$

By testing (36) with a constant and integrating, we get

$$z_N n_N^0(\infty) \int_{Y_F} e^{-z_N\xi_0(y)} \, dy = \int_S \sigma \, dS.$$

Consequently, ξ_0 solves (34) except that it is not of zero average. We have the following simple result.

Lemma 7. *Assume that σ is a smooth bounded function such that $\int_S \sigma \, dS > 0$. Then problem (36) has a unique solution $\varphi_0 \in H_\#^1(Y_F)$ such that*

$$e^{-z_N\xi_0} \qquad \text{and} \qquad e^{-z_N\xi_0}\xi_0$$

are absolutely integrable.

Case 3. $\int_S \sigma = 0$. In this case the problem corresponding to $\beta = 0$ has a solution and the analysis is much simpler.

The following limit problem

$$\begin{cases} -\Delta\Psi_0(y) = 0 \ \text{ in } \ Y_F, \\ \nabla\Psi_0 \cdot \boldsymbol{n} = -\sigma \ \text{ on } \ S, \\ \Psi_0 \ \text{ is } 1 - \text{periodic and } \int_{Y_F} \Phi(\Psi_0) \, dy = 0, \end{cases} \tag{37}$$

has a unique solution Ψ_0 since the function Φ is monotone. Then we have

$$\Psi_\beta(y) = \Psi_0(y) + O(\beta). \tag{38}$$

4.2. Rigorous perturbation results when $\int_S \sigma \, dS \neq 0$

We focus on the case $\int_S \sigma \, dS < 0$: the opposite one, $\int_S \sigma \, dS > 0$, is completely analogous. Motivated by the discussion leading to (31), we look for Ψ_β in the form

$$\Psi_\beta(y) = \frac{\log \beta}{z_1} + \varphi_\beta(y), \tag{39}$$

where φ_β is the solution of

$$\begin{cases} -\Delta \varphi_\beta(y) - z_1 n_1^0(\infty) e^{-z_1 \varphi_\beta(y)} + \tilde{\Phi}(\varphi_\beta) = 0 \ \text{ in } Y_F, \\ \nabla \varphi_\beta \cdot \boldsymbol{n} = -\sigma \ \text{ on } S, \\ \varphi_\beta \ \text{ is } 1 - \text{periodic}, \end{cases} \tag{40}$$

with

$$\tilde{\Phi}(g) = -\sum_{j=2}^{N} z_j n_j^0(\infty) \beta^{1-z_j/z_1} e^{-z_j g}. \tag{41}$$

We start with a uniform H^1-estimate for φ_β.

Lemma 8. *Let σ be a smooth bounded function such that $\int_S \sigma \, dS < 0$. Then, for small enough β, the solution φ_β of (40) satisfies the estimate*

$$\|\varphi_\beta\|_{H^1(Y_F)} \leqslant C, \tag{42}$$

where C is independent of β.

Proof. The variational formulation of problem (40) reads, for any smooth 1-periodic function φ,

$$\int_{Y_F} \nabla \varphi_\beta \cdot \nabla \varphi \, dy + \int_{Y_F} \left(\tilde{\Phi}(\varphi_\beta) - z_1 n_1^0(\infty) e^{-z_1 \varphi_\beta} \right) \varphi \, dy + \int_S \sigma \varphi \, dS = 0. \tag{43}$$

In (43) we take $\varphi = \varphi_\beta = \varphi_\beta^+ + \varphi_\beta^-$ and we get

$$\int_{Y_F} |\nabla \varphi_\beta^+|^2 \, dy + (z_1)^2 n_1^0(\infty) \int_{Y_F} |\varphi_\beta^+|^2 \, dy + \beta \Phi \left(\frac{\log \beta}{z_1} \right) \mathcal{M}(\varphi_\beta^+)$$
$$+ \int_S \sigma \varphi_\beta^+ \, dS + \int_{Y_F} |\nabla \varphi_\beta^-|^2 \, dy + \beta \Phi \left(\frac{\log \beta}{z_1} \right) \mathcal{M}(\varphi_\beta^-)$$
$$+ \int_S \sigma (\varphi_\beta^- - \mathcal{M}(\varphi_\beta^-)) \, dS + \left(\int_S \sigma \, dS \right) \mathcal{M}(\varphi_\beta^-) \leqslant 0. \tag{44}$$

Indeed,

$$\int_{Y_F} |\nabla \varphi_\beta|^2 \, dy = \int_{Y_F} |\nabla \varphi_\beta^+|^2 \, dy + \int_{Y_F} |\nabla \varphi_\beta^-|^2 \, dy, \tag{45}$$

and

$$\int_S \sigma \varphi_\beta \, dS = \int_S \sigma \varphi_\beta^+ \, dS + \int_S \sigma (\varphi_\beta^- - \mathcal{M}(\varphi_\beta^-)) \, dS + \left(\int_S \sigma \, dS \right) \mathcal{M}(\varphi_\beta^-). \tag{46}$$

Furthermore, both functions $\tilde{\Phi}(g)$ and $g \to -z_1 e^{-z_1 g}$ are monotone and

$$\tilde{\Phi}(0) - z_1 n_1^0(\infty) = \beta \Phi \left(\frac{\log \beta}{z_1} \right).$$

Thus, we deduce

$$\left(\tilde{\Phi}(\varphi_\beta) - z_1 n_1^0(\infty) e^{-z_1 \varphi_\beta} - \tilde{\Phi}(0) + z_1 n_1^0(\infty)\right) \varphi_\beta \geqslant 0. \tag{47}$$

We use a further argument of strict monotonicity for $-z_1 e^{-z_1 g}$, namely

$$\left(-z_1 n_1^0(\infty) e^{-z_1 \varphi_\beta} + z_1 n_1^0(\infty)\right) \varphi_\beta^+ = \left(-z_1 n_1^0(\infty) e^{-z_1 \varphi_\beta^+} + z_1 n_1^0(\infty)\right) \varphi_\beta^+$$
$$\geqslant (z_1)^2 n_1^0(\infty) \varphi_\beta^+, \tag{48}$$

because $\left(-z_1 e^{-z_1 g}\right)' = (z_1)^2 e^{-z_1 g} \geqslant (z_1)^2$ for $g \geqslant 0$. Equalities (45), (46), together with the lower bounds (47), (48), applied to the variational formulation (43), yield the desired inequality (44). We recall that

$$\lim_{\beta \to 0^+} \beta \Phi\left(\frac{\log \beta}{z_1}\right) = -z_1 n_1^0(\infty) > 0,$$

so that, for sufficiently small $\beta > 0$, $\beta \Phi(\frac{\log \beta}{z_1})$ is a positive bounded constant. Further, the product $(\int_S \sigma \, dS) \mathcal{M}(\varphi_\beta^-)$ is nonnegative. Therefore it suffices to apply Poincaré inequality and (42) follows. $\qquad\square$

Next we need a uniform L^∞-bound for φ_β, as β goes to 0. (Recall that the L^∞-bounds of proposition 3 are not uniform with respect to β.)

Proposition 9. *For sufficiently small $\beta > 0$, we have the bounds*

$$U(y) - U_m - \frac{1}{z_1} \log \max\left\{1, \frac{\overline{\sigma}}{z_1 n_1^0(\infty)}\right\} \geqslant \varphi_\beta(y) \geqslant$$
$$U(y) - U_M - \frac{1}{z_1} \log \min\left\{1, \frac{\overline{\sigma}}{z_1 n_1^0(\infty)}\right\}, \tag{49}$$

where U is the solution of the Neumann problem (18).

Proof. We start with the variational formulation for $\varphi_\beta - U$ which reads, for any smooth 1-periodic function φ,

$$\int_{Y_F} \nabla(\varphi_\beta - U) \cdot \nabla \varphi \, dy - z_1 n_1^0(\infty) \int_{Y_F} e^{-z_1 \varphi_\beta} \varphi \, dy + \int_{Y_F} \tilde{\Phi}(\varphi_\beta) \varphi \, dy$$
$$+ \overline{\sigma} \int_{Y_F} \varphi \, dy = 0. \tag{50}$$

We take $\varphi(y) = (\varphi_\beta(y) - U(y) + C)^-$, where C is a constant to be determined. By virtue of lemma 2, $\varphi \in H_\#^1(Y_F)$ and $\Phi(\varphi_\beta)\varphi$ is integrable. Since the function $g \to -z_j e^{-z_j g}$ and $g \to \tilde{\Phi}(g)$ are monotone, we deduce from (50)

$$\int_{Y_F} |\nabla \varphi|^2 \, dy + \int_{Y_F} \left(-z_1 n_1^0(\infty) e^{-z_1(U-C)} + \tilde{\Phi}(U-C) + \overline{\sigma}\right) \varphi \, dy \leqslant 0.$$

Hence we want to choose C such that the expression in front of φ in the second integral is nonpositive. We have

$$-z_1 n_1^0(\infty) e^{-z_1(U(y)-C)} + \tilde{\Phi}(U(y) - C) + \overline{\sigma} \leqslant$$
$$-z_1 n_1^0(\infty) e^{-z_1(U_M - C)} - \sum_{z_1 < z_j < 0} \beta^{1-z_j/z_1} z_j n_j^0(\infty) e^{-z_j(U_M - C)} + \overline{\sigma}. \tag{51}$$

Now if

$$\overline{\sigma} < z_1 n_1^0(\infty) < 0,$$

we take $C = U_M$ and the left hand side of (51) is nonpositive for β sufficiently small because the sum in (51) is small. If not, then our choice is

$$C > U_M + \frac{1}{z_1} \log \left(\frac{\overline{\sigma}}{z_1 n_1^0(\infty)} \right) > U_M.$$

This choice of the constant C implies that $\varphi(y) = 0$, for small enough β, and yields the lower bound in (49).

For the upper bound we take $\varphi(y) = (\varphi_\beta(y) - U(y) - C)^+$, where C is a constant to be determined. It yields

$$\int_{Y_F} |\nabla \varphi|^2 \, \mathrm{d}y + \int_{Y_F} \left(-z_1 n_1^0(\infty) \mathrm{e}^{-z_1(U+C)} + \tilde{\Phi}(U+C) + \overline{\sigma} \right) \varphi \, \mathrm{d}y \leqslant 0.$$

Hence we should choose C such that the expression in front of φ in the second integral is nonnegative. We have

$$- z_1 n_1^0(\infty) \mathrm{e}^{-z_1(U(y)+C)} + \tilde{\Phi}(U+C) + \overline{\sigma} \geqslant$$
$$-z_1 n_1^0(\infty) \mathrm{e}^{-z_1(U_m+C)} - \sum_{j \in j^+} \beta^{1-z_j/z_1} z_j n_j^0(\infty) \mathrm{e}^{-z_j(U_m+C)} + \overline{\sigma}. \tag{52}$$

Now if

$$z_1 n_1^0(\infty) < \overline{\sigma} < 0,$$

we choose $C = -U_m$ and, for sufficiently small β, the right hand side of (52) is positive because the sum over $j \in j^+$ is small and the expression in front of φ in the second integral is nonnegative. Otherwise, we choose

$$C > -U_m - \frac{1}{z_1} \log \left(\frac{\overline{\sigma}}{z_1 n_1^0(\infty)} \right) > -U_m$$

and, again, for sufficiently small β, the right hand side of (52) is positive, which implies the upper bound in (49). $\qquad \square$

As an immediate consequence of proposition 9, taking the limit as β goes to 0, we obtain the following corollary.

Corollary 10. *Let φ_0 be the solution of (32). It satisfies the L^∞-estimate*

$$U(y) - U_m - \frac{1}{z_1} \log \max \left\{ 1, \frac{\overline{\sigma}}{z_1 n_1^0(\infty)} \right\} \geqslant \varphi_0(y) \geqslant$$
$$U(y) - U_M - \frac{1}{z_1} \log \min \left\{ 1, \frac{\overline{\sigma}}{z_1 n_1^0(\infty)} \right\}. \tag{53}$$

Theorem 11. *We have*

$$\|\varphi_\beta - \varphi_0\|_{C^k(\bar{Y}_F)} \leqslant C \beta^{1-z_2/z_1}, \tag{54}$$

for every positive integer k. Furthermore, let φ_1 be the solution for

$$\begin{cases} -\Delta \varphi_1 + (z_1)^2 n_1^0(\infty) \mathrm{e}^{-z_1 \varphi_0} \varphi_1 = z_2 n_2^0(\infty) \mathrm{e}^{-z_2 \varphi_0} & \text{in } Y_F, \\ \nabla \varphi_1 \cdot \boldsymbol{n} = 0 & \text{on } S, \\ \varphi_1 \text{ is } 1 - periodic. \end{cases} \tag{55}$$

Then, for every positive integer k, we have

$$\|\varphi_\beta - \varphi_0 - \beta^{1-z_2/z_1} \varphi_1\|_{C^k(\bar{Y}_F)} \leqslant C \beta^q, \tag{56}$$

where $0 < q = \min(1 - z_3/z_1, \, 2(1 - z_2/z_1))$.

Proof. First we observe that $\varphi_\beta - \varphi_0$ satisfies the variational equation

$$\int_{Y_F} \nabla(\varphi_\beta - \varphi_0) \cdot \nabla\varphi \, dy - z_1 n_1^0(\infty) \int_{Y_F} (e^{-z_1\varphi_\beta} - e^{-z_1\varphi_0})\varphi \, dy =$$

$$-\int_{Y_F} \tilde{\Phi}(\varphi_\beta)\varphi \, dy \text{ for all smooth 1-periodic } \varphi. \tag{57}$$

Now we take $\varphi = \varphi_\beta - \varphi_0$ as a test function, use the strict monotonicity of the function $g \to -z_j e^{-z_j g}$, the L^∞-bounds (49) and (53) to conclude that

$$\|\varphi_\beta - \varphi_0\|_{H^1(Y_F)} \leqslant C\beta^{1-z_2/z_1}. \tag{58}$$

Next we write the equation for $\varphi_\beta - \varphi_0$ as

$$\begin{cases} -\Delta(\varphi_\beta - \varphi_0) + (\varphi_\beta - \varphi_0) = (\varphi_\beta - \varphi_0) \\ +z_1 n_1^0(\infty)(e^{-z_1\varphi_\beta} - e^{-z_1\varphi_0}) - \tilde{\Phi}(\varphi_\beta) \text{ in } Y_F, \\ \nabla(\varphi_\beta - \varphi_0) \cdot \boldsymbol{n} = 0 \text{ on } S, \\ (\varphi_\beta - \varphi_0) \text{ is } 1 - \text{periodic.} \end{cases} \tag{59}$$

Using the estimate (58), we get the H^2-error estimate of the same order. After bootstrapping we obtain the required error estimate (54).

Eventually, we write the equation for $\varphi_\beta - \varphi_0 - \beta^{1-z_2/z_1}\varphi_1$ and repeating the above procedure yields (56). $\qquad\square$

Remark 12. In the frequently considered case of two ions of opposite unit charge ($N = 2$, $-z_1 = z_2 = 1$), normalizing the coefficients $n_1^0(\infty) = n_2^0(\infty) = 1$, we have

$$\Phi(g) = 2\sinh g, \qquad \varphi_\beta = \varphi_0 + \beta^2\varphi_1 + \beta^4\varphi_2 + \cdots$$

and, in the case $\int_S \sigma \, dS < 0$, the equations for the functions φ_j read

$$-\Delta\varphi_0 + e^{\varphi_0} = 0,$$
$$-\Delta\varphi_1 + e^{\varphi_0}\varphi_1 = e^{-\varphi_0},$$
$$-\Delta\varphi_2 + e^{\varphi_0}\varphi_2 = -e^{\varphi_0}\varphi_1^2 - e^{-\varphi_0}\varphi_1$$

and we have

$$\|\varphi_\beta - \varphi_0 - \beta^2\varphi_1 - \beta^4\varphi_2\|_{C^k(\bar{Y}_F))} \leqslant C\beta^6, \tag{60}$$

for every positive integer k.

The case $\int_S \sigma \, dS > 0$ is analogous and it is enough to repeat the above strategy with z_1 replaced with z_N.

4.3. Rigorous perturbation results in the case $\int_S \sigma \, dS = 0$

Here the proofs are much simpler than in the previous subsection. We just state the results. Again, the starting point are the uniform H^1-estimate for Ψ_β.

Lemma 13. *Let σ be a smooth function such that $\int_S \sigma \, dS = 0$. Then the solution Ψ_β of problem (10) satisfies the uniform estimates*

$$U(y) - U_m - \frac{1}{z_1}\log\max\left(1, -\sum_{j\in j^+}\frac{z_j n_j^0(\infty)}{z_1 n_1^0(\infty)}\right) \geqslant \Psi(y) \geqslant$$

$$U(y) - U_M - \frac{1}{z_N}\log\max\left(1, -\sum_{j\in j^-}\frac{z_j n_j^0(\infty)}{z_N n_N^0(\infty)}\right), \tag{61}$$

and

$$\|\Psi_\beta\|_{H^1(Y_F)} \leqslant C, \tag{62}$$

where C is independent of β.

Proof. The L^∞-bound (61) is a direct consequence of proposition 3. Note that (61) is uniform with respect to β. To obtain (62) we take the test function $\varphi = \Psi_\beta$ in the variational formulation (24)

$$\int_{Y_F} |\nabla\Psi_\beta|^2 \, \mathrm{d}y + \beta \int_{Y_F} \Phi(\Psi_\beta)\Psi_\beta \, \mathrm{d}y + \int_S \sigma\Psi_\beta \, \mathrm{d}S = 0.$$

Since Φ is monotone and satisfies $\Phi(0) = 0$, we have $\Phi(\Psi_\beta)\Psi_\beta \geqslant 0$, while the assumption $\int_S \sigma \, \mathrm{d}S = 0$ implies that

$$\int_S \sigma\Psi_\beta \, \mathrm{d}S = \int_S \sigma\left(\Psi_\beta - \mathcal{M}(\Psi_\beta)\right) \, \mathrm{d}S \leqslant C\|\sigma\|_{L^2(S)}\|\nabla\Psi_\beta\|_{L^2(Y_F)}$$

by virtue of the Poincaré–Wirtinger inequality. We thus deduce

$$\|\nabla\Psi_\beta\|_{L^2(Y_F)} \leqslant C\|\sigma\|_{L^2(S)},$$

which, together with (61), implies (62). $\qquad\square$

In section 4.1 we already introduced the limit problem (37) for $\Psi_0 = \lim_{\beta\to 0}\Psi_\beta$. We can also define a corrector Ψ_1 as the unique solution of

$$\begin{cases} -\Delta\Psi_1(y) = -\Phi(\Psi_0) \text{ in } Y_F, \\ \nabla\Psi_1 \cdot \boldsymbol{n} = 0 \text{ on } S, \\ \Psi_1 \text{ is } 1 - \text{periodic and } \displaystyle\int_{Y_F} \Phi'(\Psi_0)\Psi_1 \, \mathrm{d}y = 0. \end{cases} \tag{63}$$

There exists a solution of (63) because $\int_{Y_F} \Phi(\Psi_0) \, \mathrm{d}y = 0$ as required by the definition of (37). As an obvious consequence of lemma 13 we get the following error estimate.

Theorem 14. *Let Ψ_0 be the solution of (37) and Ψ_1 that of (63). Then we have*

$$\|\Psi_\beta - \Psi_0\|_{C^k(\bar{Y}_F)} \leqslant C\beta, \qquad \|\Psi_\beta - \Psi_0 - \beta\Psi_1\|_{C^k(\bar{Y}_F)} \leqslant C\beta^2, \tag{64}$$

for every positive integer k.

The proof of theorem 14 follows the lines of the proof of theorem 11.

5. Large β limit

We now investigate the asymptotic behaviour of Ψ_β when the β parameter goes to $+\infty$. In view of its definition (5), a large value of β corresponds either to a large pore size L or to a small Debye length λ_D, but also to a large common value of the concentrations $n_j^0(\infty)$. A similar asymptotic analysis has been performed in [2, 18] in one space dimension. In higher space dimensions our main tool to obtain the behaviour near the solid boundaries is the multidimensional boundary layer technique introduced by Vishik and Lyusternik [25] (which was originally introduced for linear problems).

5.1. Formal asymptotics

In the PB system (10) the parameter β appears in the partial differential equation but not in the Neumann boundary condition. This indicates the presence of boundary layers in the asymptotic analysis, the thickness of which shall be of the order of $O(1/\beta)$. The usual technique to handle this situation is that of matched asymptotic expansion. We first consider an outer expansion of the solution Ψ_β in Y_F, away from the boundary S. In a second step we shall construct an inner expansion of Ψ_β in the vicinity of S, which is equivalently a boundary layer.

We begin with the outer expansion for Ψ_β which reads

$$\Psi_\beta = \Psi_\infty + \frac{1}{\beta}\Psi_{1,\infty} + \frac{1}{\beta^2}\Psi_{2,\infty} + \cdots .$$

After plugging this ansatz in the PB equation (10) we get

$$-\frac{1}{\beta}\Delta\Psi_\beta + \Phi(\Psi_\beta) = \Phi(\Psi_\infty) + \frac{1}{\beta}\Big(\Phi'(\Psi_\infty)\Psi_{1,\infty} - \Delta\Psi_\infty\Big) + \ldots = 0 \ \text{ in } \ Y_F$$

which implies, at the zero order, that $\Phi(\Psi_\infty) = 0$. The electroneutrality condition (16) tells us that 0 is the unique root of the monotone function Φ. Therefore we deduce $\Psi_\infty = 0$ in Y_F. In other words we have

$$\Psi_\beta(y) = O\left(\frac{1}{\beta}\right) \qquad \text{in } Y_F, \text{ away from the boundary } S. \tag{65}$$

In fact we will check rigorously in the following subsection that this order of magnitude holds for the L^1-norm of Ψ_β.

We now turn to the inner expansion of Ψ_β, i.e. its behaviour close to S, which is more complicated. We study it locally near a point $y_0 \in S$, using the geometrical setting introduced in section 3.1. We consider a tubular neighbourhood Y_F^μ of S with μ small but much bigger than $\beta^{-1/2}$. Locally, in a neighbourhood $\mathcal{N}(y_0)$ of y_0, we make the change of variables $y \rightarrow q = (q', q_d)$, as defined in section 3.1, which satisfies $|\nabla_y q_d| = 1$ in $\mathcal{N}(y_0)$ and $\boldsymbol{n} \cdot \nabla_y q_d = 1$ on $\mathcal{N}(y_0) \cap S$. The Jacobian J (corresponding to the volume differential change $\mathrm{d}y = J\mathrm{d}q$) is defined by

$$J = \det\left(\frac{\partial y_k}{\partial q_j}\right)_{1\leqslant j,k\leqslant d}, \tag{66}$$

and the metric matrix (corresponding to the transformation $y \rightarrow q$)

$$K = \left(\sum_{j=1}^{d} \frac{\partial q_k}{\partial y_j}\frac{\partial q_r}{\partial y_j}\right)_{1\leqslant k,r\leqslant d}, \tag{67}$$

which satisfies

$$K_{d,d} = 1, \qquad K_{k,d} = 0 \qquad \text{for } 1 \leqslant k \leqslant d-1.$$

Note that the coordinates $q = q(y)$ are introduced in such a way that the level sets $\{q_d = \text{const}\}$ and the normal lines $\{q' = (C_1, \ldots, C_{d-1}\}$ are orthogonal (that is the corresponding tangential hyperplanes and lines are orthogonal). Since $\nabla_y q_d(y)$ gives the direction of the normal line and $\nabla_y q_k$, $k = 1, 2, \ldots, d-1$, form a basis in the tangential hyperplane, we have $K_{k,d} = \nabla_y q_k \cdot \nabla_y \text{dist}(y, S) = 0$ for $k \neq d$.

Differential operators in new coordinates transform as follows:

$$\frac{\partial}{\partial y_j} = \sum_{k=1}^{d} \frac{\partial q_k}{\partial y_j}\frac{\partial}{\partial q_k}, \qquad j = 1, \ldots, d;$$

$$\sum_{k=1}^{d} \frac{\partial^2}{\partial y_k^2} = \frac{1}{J}\text{div}_q\left(J\,K\,\nabla_q\right) \qquad \text{in } Y_F^\mu \cap \mathcal{N}(y_0); \tag{68}$$

$$\boldsymbol{n} \cdot \nabla_y = -\frac{\partial}{\partial q_d} \qquad \text{on } S. \tag{69}$$

Applying this change of variables to the variational formulation (24) of the PB system (10) yields the following equation in the new coordinates

$$-\operatorname{div}_q \left(J\, K\, \nabla_q \Psi_\beta \right) + \beta\, J\, \Phi(\Psi_\beta) = 0. \tag{70}$$

Dividing (70) by J yields that the partial differential equation in $Y_F^\mu \cap \mathcal{N}(y_0)$ and the boundary condition on $S \cap \mathcal{N}(y_0)$ of (10) transform into

$$-\frac{\partial^2 \Psi_\beta}{\partial q_d^2} + \beta\Phi(\Psi_\beta) + \text{ lower order derivatives in } q_d$$

$$+ \text{ second order differential operator in } q' \ = \ 0 \text{ in } Y_F^\mu \cap \mathcal{N}(y_0), \tag{71}$$

$$\frac{\partial \Psi_\beta}{\partial q_d} = \sigma \ \text{ on } S \cap \mathcal{N}(y_0). \tag{72}$$

As usual in the method of matched asymptotic expansions, problem (71)–(72) serves to construct the inner expansion. Since we expect the thickness of the boundary layer to be of order $O(1/\beta)$, we search for the inner expansion of the form

$$\Psi_\beta(q', q_d) = \beta^{-1/2} \sum_{j=0}^{\infty} \beta^{-j/2} \Psi_j(q', \beta^{1/2} q_d). \tag{73}$$

Expanding the zero-order term $\Phi(\Psi_\beta)$ in Taylor series and taking into account the bulk electroneutrality condition (16), $\Phi(0) = 0$, we obtain

$$\Phi(\Psi_\beta) = -\sum_{k=1}^{N} z_k n_k^0(\infty) e^{-z_k \Psi_\beta} = \Phi'(0)\Psi_\beta + \frac{1}{2}\Phi''(0)(\Psi_\beta)^2 + \cdots$$

$$= \beta^{-1/2} \sum_{k=1}^{N} z_k^2 n_k^0(\infty)\Psi_0 + \beta^{-1} \sum_{k=1}^{N} z_k^2 n_k^0(\infty)\left(\Psi_1 - \frac{1}{2} z_k (\Psi_0)^2\right) + \cdots. \tag{74}$$

Introducing $\xi = \beta^{1/2} q_d$, substituting (73) and (74) in (71)–(72) and collecting power-like terms in the resulting equations, after straightforward rearrangements we arrive at the following problem for the main term of the expansion:

$$\frac{d^2}{d\xi^2}\Psi_0(q', \xi) - \left(\sum_{k=1}^{N} z_k^2 n_k^0(\infty)\right)\Psi_0(q', \xi) = 0 \qquad \text{for } \xi > 0; \tag{75}$$

$$\frac{d}{d\xi}\Psi_0(q', 0) = \sigma(q') \qquad \text{for } \xi = 0. \tag{76}$$

Problem (75)–(76) is a second-order ordinary differential equation on the positive half-line. After matching with the outer solution $\Psi_\beta = O(\frac{1}{\beta})$, we impose additionally that $\Psi_0(q', +\infty) = 0$. The exact solution of (75)–(76) is thus

$$\Psi_0(q', \xi) = \frac{-\sigma(q')}{\sqrt{\Phi'(0)}} \exp\{-\xi\sqrt{\Phi'(0)}\}, \tag{77}$$

with $\Phi'(0) = \sum_{k=1}^{N} z_k^2 n_k^0(\infty)$. Returning to the original variables, we get

$$\Psi_\beta(y) = \frac{-\sigma(y)}{\sqrt{\beta\Phi'(0)}} \exp\{-d(y)\sqrt{\beta\Phi'(0)}\} + O\left(\frac{1}{\beta}\right), \tag{78}$$

where $d(y)$ is the distance between y and S. This asymptotic expansion (78) will be justified rigorously in the next subsection.

Remark 15. The above expressions can be simplified if we specify our choice of the characteristic concentration n_c. Specifically, taking $n_c = \sum_{k=1}^{N} z_k^2 n_k^*(\infty)$ we obtain that $\sum_{k=1}^{N} z_k^2 n_k^0(\infty) = 1$ or equivalently $\Phi'(0) = 1$.

5.2. Rigorous error estimate

In the case of constant ζ, we start with two useful simple inequalities for the nonlinearity Φ.

Lemma 16. *Let Φ be given by (11), i.e. $\Phi(x) = -\sum_{k=1}^{N} z_k n_k^0(\infty) e^{-z_k x}$. There exist positive constants H, C_0, C_k such that, $\forall x \in \mathbb{R}$,*

$$\Phi(x) \operatorname{sign}(x) \geqslant H^2 |x|, \tag{79}$$

$$\Phi'(x) \geqslant C_0 + C_k |x|^{k-2}, \qquad k \geqslant 2. \tag{80}$$

Proof. To prove (80) we note that

$$\Phi'(x) \geqslant (z_1)^2 n_1^0(\infty) e^{-z_1 x} + (z_N)^2 n_N^0(\infty) e^{-z_N x}$$

with $z_1 < 0 < z_N$, which implies the desired result. Then (79) follows from a Taylor expansion of $\Phi(x)$ at 0 and the bulk electroneutrality condition (16), $\Phi(0) = 0$. $\square$

We now prove *a priori* estimates which improve that of lemma 5.

Lemma 17. *Let Ψ_β be the unique solution of (10). There exists a positive constant C such that, $\forall \beta \geqslant 1$,*

$$\|\Psi_\beta\|_{L^1(Y_F)} \leqslant \frac{C}{\beta}, \tag{81}$$

$$\|\Psi_\beta\|_{L^k(Y_F)} \leqslant C\beta^{-3/(2k)}, \qquad k \geqslant 2, \tag{82}$$

$$\|\Psi_\beta\|_{H^1(Y_F)} \leqslant C\beta^{-1/4}. \tag{83}$$

Proof. First, in the variational formulation (24) we use the test function $\varphi = \Psi_\beta$. It yields

$$\int_{Y_F} |\nabla \Psi_\beta|^2 \, \mathrm{d}y + \beta \int_{Y_F} \Phi(\Psi_\beta) \Psi_\beta \, \mathrm{d}y = -\int_S \sigma \Psi_\beta \, \mathrm{d}S. \tag{84}$$

Since $\beta \geqslant 1$ and $\Phi(x)x \geqslant H^2 |x|^2$ because of (79), we deduce from (84) that $\|\Psi_\beta\|_{H^1(Y_F)} \leqslant C$ (this estimate will be improved later). Second, in the variational formulation (24) we use a test function which is a (monotone) regularization of the sign of Ψ_β. The first term in (24) is non-negative and the right hand side is bounded thanks to the previous estimate. Thus, after passing to the regularization parameter limit, we get

$$\beta \int_{Y_F} \Phi(\Psi_\beta) \operatorname{sign}(\Psi_\beta) \, \mathrm{d}y \leqslant C,$$

and after applying inequality (79) we get (81). Next, we consider again (84) where the nonlinear term is bounded from below using inequality (80)

$$\beta \int_{Y_F} \Phi(\Psi_\beta) \Psi_\beta \, \mathrm{d}y \geqslant \beta \left(C_0 \int_{Y_F} |\Psi_\beta|^2 \, \mathrm{d}y + C_k \int_{Y_F} |\Psi_\beta|^k \, \mathrm{d}y \right). \tag{85}$$

Furthermore, using a trace inequality [13], we get

$$\left| \int_S \sigma \Psi_\beta \, \mathrm{d}S \right| \leqslant C \|\Psi_\beta\|_{L^2(S)} \leqslant C \|\Psi_\beta\|_{H^1(Y_F)}^{1/2} \|\Psi_\beta\|_{L^2(Y_F)}^{1/2}$$

$$\leqslant C \left(\beta\delta \|\Psi_\beta\|_{L^2(Y_F)}^2 + (\beta\delta)^{-1/3} \|\Psi_\beta\|_{H^1(Y_F)}^{2/3} \right), \tag{86}$$

where we used Young's inequality $ab \leqslant a^4/4 + 3b^{4/3}/4$ for $a = (\beta\delta)^{1/4}\|\Psi_\beta\|_{L^2(Y_\mathrm{F})}^{1/2}$ and $b = (\beta\delta)^{-1/4}\|\Psi_\beta\|_{H^1(Y_\mathrm{F})}^{1/2}$. For $\beta \geqslant 1$ and $\delta > 0$ small enough, (82)–(83) is a direct consequence of (86). $\qquad\square$

Since S is compact there exist finitely many points $y_i^0 \in S$ and neighbourhoods $\mathcal{N}(y_i^0)$, $1 \leqslant i \leqslant M$, such that the open sets $W_i = Y_\mathrm{F} \cap \mathcal{N}(y_i^0)$ cover S, i.e. $S \subset \cup_{i=1}^M \overline{W}_i$. Take $W_0 \subset\subset Y_\mathrm{F}$ so that $Y_F \subset \cup_{i=0}^M W_i$ and let $\{\zeta_i\}_{i=0}^M$ be an associated partition of unity. Here Y_F and S are considered as subsets of the unit torus $\mathbb{T}^d$, so the functions $\zeta_i(y)$ are 1-periodic.

Proposition 18. *In each set $q(W_i)$ (the image of W_i by the map $y \to q$) define a boundary layer function*

$$\psi_i^{bl}(q) = \beta^{-1/2}\Psi_0(q', \beta^{1/2}q_d) = \frac{-\sigma(q')}{\sqrt{\beta\Phi'(0)}}\exp\{-q_d\sqrt{\beta\Phi'(0)}\}, \qquad (87)$$

where Ψ_0 is defined by (77). For any smooth test function φ, such that $\varphi = 0$ on $\partial q(W_i) \setminus q(S \cap W_i)$, it satisfies

$$\int_{q(W_i)} K^i \nabla_q \psi_i^{bl} \cdot \nabla_q \varphi \, J^i \, \mathrm{d}q + \beta \int_{q(W_i)} \Phi(\psi_i^{bl})\varphi \, J^i \, \mathrm{d}q$$
$$+ \int_{q(S\cap W_i)} \sigma\varphi\sqrt{1 + |\nabla_{q'}\gamma_i|^2} \, \mathrm{d}q' = \int_{q(W_i)} R_\beta^i \varphi \, \mathrm{d}q, \qquad (88)$$

where J^i is the Jacobian of the map $y \to q$, defined by (66), K^i is the metric matrix defined by (67) and

$$\|R_\beta^i\|_{L^\infty(q(W_i))} \leqslant C, \qquad \|R_\beta^i\|_{L^1(q(W_i))} \leqslant \frac{C}{\sqrt{\beta}}. \qquad (89)$$

Proof. The proof is found by direct calculations, using the explicit formula (87) and taking into account that $K_{k,d}^i = 0$ for $1 \leqslant k \leqslant d - 1$. $\qquad\square$

Now, considering the boundary layers ψ_i^{bl} as functions of y, we immediately obtain the following corollary.

Corollary 19. *The boundary layers $\psi_i^{bl}(q(y))$ satisfy, for any $\varphi \in H^1(W_i)$,*

$$\int_{W_i} \nabla_y(\zeta_i\psi_i^{bl}) \cdot \nabla_y\varphi \, \mathrm{d}y + \beta \int_{W_i} \Phi(\zeta_i\psi_i^{bl})\varphi \, \mathrm{d}y + \int_{S\cap W_i} \zeta_i\sigma\varphi \, \mathrm{d}S = \int_{W_i} R_\beta^i \varphi \, \mathrm{d}y, \qquad (90)$$

where the redefined remainders R_β^i satisfy

$$\|R_\beta^i\|_{L^\infty(W_i)} \leqslant C, \qquad \|R_\beta^i\|_{L^1(W_i)} \leqslant \frac{C}{\sqrt{\beta}}. \qquad (91)$$

Due to the geometric assumptions from section 3.1, for μ sufficiently small, the tubular neighbourhood $Y_\mathrm{F}^\mu = \{y \in Y_\mathrm{F} : \mathrm{dist}(y, S) < \mu\}$ satisfies $Y_\mathrm{F}^\mu \subset \cup_{i=1}^M W_i$.

An arbitrary smooth function f, defined on Y_F is then written as $f = \sum_{i=1}^M \zeta_i f + \zeta_0 f$. The boundary between Y_F^μ and $Y_\mathrm{F} \setminus \overline{Y}_F^\mu$ is C^3 and we extend smoothly f from Y_F^μ into $Y_\mathrm{F} \setminus \overline{Y}_F^\mu$. In $Y_\mathrm{F} \setminus \overline{Y}_F^\mu$, f, together with its derivatives, is exponentially small with respect to $1/\beta$.

In the calculations which follow we replace f by the above extension of $\sum_{i=1}^M \zeta_i f$ from Y_F^μ to Y_F. The error is exponentially small in $1/\sqrt{\beta}$ and we ignore it.

Collecting together the boundary layers with the associated partition of unity, we define

$$\psi^{bl} = \sum_{i=1}^M \zeta_i \psi_i^{bl} \qquad (92)$$

and deduce the following result.

Proposition 20. *For any $\varphi \in H^1_\#(Y_F)$, we have*

$$\int_{Y_F} \nabla(\Psi_\beta - \psi^{bl}) \cdot \nabla\varphi \, dy + \beta \int_{Y_F} \left(\Phi(\Psi_\beta) - \Phi(\psi^{bl}) \right) \varphi \, dy = \int_{Y_F} R_\beta \varphi \, dy, \tag{93}$$

where the global remainder R_β satisfies

$$\|R_\beta\|_{L^\infty(Y_F)} \leqslant C, \qquad \|R_\beta\|_{L^1(Y_F)} \leqslant \frac{C}{\sqrt{\beta}}. \tag{94}$$

Proof. We obtain (93) by subtracting the variational formulations (90) of the boundary layers ψ^{bl}_i from the variational formulation (24) of Ψ_β. We use the fact that

$$\Phi\left(\sum_{i=1}^M \zeta_i \psi^{bl}_i \right) = \sum_{i=1}^M \zeta_i \Phi(\psi^{bl}_i) + O(\beta^{-1/2})$$

since $\psi^{bl}_i = O(\beta^{-1/2})$ and $\Phi(0) = 0$. □

Finally we obtain the main result of this section which is a rigorous justification of (78) (recall that $\psi^{bl}_i(q) = \beta^{-1/2}\Psi_0(q', \beta^{1/2}q_d)$).

Theorem 21. *Let Ψ_β be the unique solution of (10) and ψ^{bl} be given by (92). There exists a positive constant C such that, $\forall \beta \geqslant 1$,*

$$\|\Psi_\beta - \psi^{bl}\|_{L^1(Y_F)} \leqslant \frac{C}{\beta^{3/2}}, \tag{95}$$

$$\|\Psi_\beta - \psi^{bl}\|_{L^2(Y_F)} \leqslant \frac{C}{\beta^{5/4}}, \tag{96}$$

$$\|\Psi_\beta - \psi^{bl}\|_{H^1(Y_F)} \leqslant \frac{C}{\beta^{3/4}}. \tag{97}$$

Proof. The proof is similar to that of lemma 17. First, we test (93) by the regularized sign of $\Psi_\beta - \psi^{bl}$. After passing to the regularization parameter limit and using the second inequality of (94), we get

$$\beta \int_{Y_F} \left(\Phi(\Psi_\beta) - \Phi(\psi^{bl}) \right) \, \mathrm{sign}\left(\Psi_\beta - \psi^{bl} \right) \mathrm{d}y \leqslant \frac{C}{\sqrt{\beta}},$$

Since (80) implies that $\Phi'(x) \geqslant C > 0$, we deduce (95).

Next we test (93) by $\Psi_\beta - \psi^{bl}$. It yields

$$\int_{Y_F} |\nabla(\Psi_\beta - \psi^{bl})|^2 \, dy + \beta \int_{Y_F} \left(\Phi(\Psi_\beta) - \Phi(\psi^{bl}) \right) (\Psi_\beta - \psi^{bl}) \, dy$$

$$\leqslant \|R_\beta\|_{L^\infty(Y_F)} \|\Psi_\beta - \psi^{bl}\|_{L^1(Y_F)} \leqslant \frac{C}{\beta^{3/2}}. \tag{98}$$

For $\beta \geqslant 1$, (96)–(97) is a direct consequence of (98). □

Theorem 21 justifies the approximation (78) by providing error estimates in integral norms. The next result gives pointwise estimates for the same asymptotic approximation.

Lemma 22. *There exist positive constants β_0, C_1 and C_2 such that, for all $\beta > \beta_0$ and for all $y \in Y_F$, the following estimates hold:*

$$|\Psi_\beta(y)| \leqslant \frac{C_1}{\sqrt{\beta}} \exp\left\{ - C_2\sqrt{\beta} \operatorname{dist}(y, S)\right\}, \tag{99}$$

$$|\nabla\Psi_\beta(y)| \leqslant C_1 \exp\left\{ - C_2\sqrt{\beta} \operatorname{dist}(y, S)\right\}, \tag{100}$$

$$|\Psi_\beta(y) - \psi^{bl}(y)| \leqslant \frac{C_1}{\beta} \exp\left\{ - C_2\sqrt{\beta} \operatorname{dist}(y, S)\right\}. \tag{101}$$

Proof. Introduce a function of $s \in \mathbb{R}$

$$p(s) = \begin{cases} \Phi(s)/s & \text{for } s \neq 0, \\ \displaystyle\sum_{j=1}^{N} z_j^2 n_j^0(\infty) & \text{for } s = 0. \end{cases}$$

From (79) in lemma 16, we deduce $p(s) \geqslant H^2 > 0$ for all $s \in \mathbb{R}$. It also readily follows from the definition of p that p is a continuous function of s.

Recall that Y_F and S are subsets of the unit torus $\mathbb{T}^d$. Therefore, 1-periodic boundary conditions are implicit for all boundary value problems below. For the sake of brevity we do not indicate them. Introducing a function $B_\beta(y) = p(\Psi_\beta(y))$ (which is continuous and satisfies $B_\beta(y) \geqslant H^2$), the PB equation (10) can be rewritten as

$$\begin{cases} -\Delta\Psi_\beta + \beta B_\beta(y)\Psi_\beta = 0, & \text{in } Y_F, \\ \nabla\Psi_\beta \cdot \boldsymbol{n} = -\sigma, & \text{on } S. \end{cases}$$

Denote $\Sigma = \|\sigma\|_{L^\infty(S)}$. Then, by the maximum principle,

$$|\Psi_\beta| \leqslant \Psi_\beta^+ \qquad \text{in } Y_F,$$

where Ψ_β^+ is the unique solution of

$$\begin{cases} -\Delta\Psi_\beta^+ + \beta H^2\Psi_\beta^+ = 0, & \text{in } Y_F, \\ \nabla\Psi_\beta \cdot \boldsymbol{n} = \Sigma, & \text{on } S. \end{cases}$$

Thus, it suffices to show that

$$|\Psi_\beta^+(y)| \leqslant \frac{C_1}{\sqrt{\beta}} \exp\left\{ - C_2\sqrt{\beta} \operatorname{dist}(y, S)\right\}, \qquad \text{for all } y \in Y_F. \tag{102}$$

In order to prove (102), we are going to construct a so-called barrier function. For any $y \in S$ denote by $R(y)$ the radius of curvature of S at y. Under our standing assumption on the smoothness of S we have $R(y) \geqslant R_0 > 0$, $\forall y \in S$. For R_0 small enough, each of the neighbourhoods $\mathcal{N}(y_i^0)$, $1 \leqslant i \leqslant M$, covering S contains a ball of centre y_i^0 and radius $(R_0/2)$. In this ball, we rewrite the Laplace operator in terms of the new coordinates $q = q(y)$, introduced in section 3.1,

$$-\Delta_y = -\frac{\partial^2}{\partial q_d^2} + \sum_{i,j=1}^{d-1} Q_{ij}(q)\frac{\partial^2}{\partial q_i \partial q_j} + \sum_{j=1}^{d} Q_j^0(q)\frac{\partial}{\partial q_j},$$

with regular bounded functions $Q_{ij}(q)$ and $Q_j^0(q)$ defined in terms of K_{ij} and J. Setting

$$\mathcal{G}(s) = \begin{cases} s - \dfrac{s^2}{R_0} & \text{if } s \leqslant \dfrac{R_0}{2}, \\ \dfrac{R_0}{4}, & \text{otherwise}, \end{cases}$$

and

$$U(y) = \frac{2\Sigma}{H\sqrt{\beta}} \exp\left\{ -\sqrt{\beta}\frac{H}{2}\mathcal{G}(q_d) \right\},$$

after straightforward computations we obtain

$$\nabla U \cdot \boldsymbol{n}\Big|_S = -\frac{\partial U}{\partial q_d}\Big|_{q_d=0} = \Sigma. \tag{103}$$

Notice also that $U \in H^2(Y_\mathrm{F})$ because $\nabla U(y) = 0$ if $\mathrm{dist}(y, S) = R_0/2$.

Substituting U in the equation yields, for all $y \in Y_\mathrm{F}$ such that $q_d \leqslant R_0/2$,

$$-\Delta U + \beta H^2 U = \beta\left\{ -\frac{H^2}{4}\left(1 - \frac{2q_d}{R_0}\right)^2 - \frac{H}{R_0\sqrt{\beta}} - \frac{Q_d^0(q)H}{2\sqrt{\beta}}\left(1 - \frac{2q_d}{R_0}\right) + H^2 \right\}U.$$

Clearly, for all sufficiently large β the above right hand side is positive. Therefore, for $\beta > \beta_0$,

$$-\Delta U + \beta H^2 U \geqslant 0 \qquad \text{in } Y_\mathrm{F}.$$

Combining this relation with (103), and using the maximum principle, we conclude that $\Psi_\beta^+ \leqslant U$ in Y_F. Since $\mathrm{dist}(y, S)$ in Y_F is bounded by some constant C_3 and $\mathcal{G}(s) \geqslant C_4 s$ for any $s \in (0, C_3)$, this implies the first desired estimate (99).

Estimate (100) follows from (99) thanks to the standard elliptic estimates. Indeed, in the rescaled coordinates $z = \sqrt{\beta}y$ equation (10) reads

$$-\Delta_z \Psi_\beta = -\Phi(\Psi_\beta) \qquad \text{in } \sqrt{\beta}Y_\mathrm{F}$$

$$\nabla_z \Psi_\beta \cdot \boldsymbol{n}_z = -\frac{1}{\sqrt{\beta}}\sigma \qquad \text{on } \sqrt{\beta}S.$$

By (99) for any ball $B_{z_0,1} = \{z : |z - z_0| \leqslant 1\}$ with $y_0 \in \sqrt{\beta}Y_\mathrm{F}$ we have

$$|\Psi_\beta(z)| \leqslant \frac{C}{\sqrt{\beta}}\mathrm{e}^{-c_2\mathrm{dist}(z_0, \sqrt{\beta}S)}, \qquad |\Phi(\Psi_\beta(z))| \leqslant \frac{C}{\sqrt{\beta}}\mathrm{e}^{-c_2\mathrm{dist}(z_0, \sqrt{\beta}S)},$$

$z \in B_{z_0,1} \cap \sqrt{\beta}Y_\mathrm{F}$. Considering our regularity assumptions on S and σ, by the local elliptic estimates for the Poisson equation including those near the boundary, we obtain

$$|\nabla_z \Psi_\beta(z)| \leqslant \frac{C}{\sqrt{\beta}}\mathrm{e}^{-c_2\mathrm{dist}(z_0, \sqrt{\beta}S)}, \qquad z \in B_{z_0,1/2} \cap \sqrt{\beta}Y_\mathrm{F}.$$

In the coordinates y this yields the desired estimate (100).

Estimate (101) can be obtained by means of similar arguments as in the proof of (99). Here we just outline the proof and leave the details to the reader. From the definition of Ψ_β and ψ^{bl} and estimate (99) it readily follows that the difference $V_\beta = \Psi_\beta - \psi^{bl}$ satisfies in Y_F^μ, $\mu = R_0/2$, the following problem:

$$-\Delta V_\beta(y) + \beta\Phi'(0)V_\beta(y) = g_1(y) \qquad \text{in } Y_\mathrm{F}^\mu,$$

$$\nabla V_\beta \cdot \boldsymbol{n}\Big|_S = 0, \qquad V_\beta\Big|_{|q_d(y)|=\frac{R_0}{2}} = g_2(y)$$

with

$$|g_1(y)| \leqslant c_1\mathrm{e}^{-c_2\sqrt{\beta}q_d(y)}, \qquad |g_2(y)| \leqslant \frac{1}{\sqrt{\beta}}c_1\mathrm{e}^{-c_2\sqrt{\beta}R_0/2} \leqslant \frac{1}{\beta}c_1\mathrm{e}^{-c_3\sqrt{\beta}R_0/2};$$

here the constants $c_2 > 0$ and $c_3 > 0$ do not depend on β. Setting $\overline{V}_\beta = \frac{C}{\beta}\mathrm{e}^{-\sqrt{\beta}H_1 q_d(y)}$ and choosing large enough $C > 0$ and small enough $H_1 > 0$, we obtain that for all sufficiently large β it holds

$$-\Delta\overline{V}_\beta + \beta\Phi'(0)\overline{V}_\beta > g_1, \qquad \nabla\overline{V}_\beta \cdot \boldsymbol{n}\Big|_S < 0, \qquad \overline{V}_\beta\Big|_{|q_d(y)|=\frac{R_0}{2}} > g_2.$$

Therefore, $V_\beta \leqslant \overline{V}_\beta$ in Y_F^μ. Similarly, $V_\beta \geqslant -\overline{V}_\beta$ in Y_F^μ. This yields (101) in Y_F^μ. In $Y_\mathrm{F} \setminus Y_\mathrm{F}^\mu$ (101) follows by the maximum principle. $\qquad\square$

6. Dirichlet boundary condition or ζ potential at the boundary

The previous asymptotic analysis was specific to the Neumann boundary condition (or given charge density σ) imposed on the pore walls S. The situation is quite different for the Dirichlet boundary condition (or ζ potential) on S. We briefly investigate this case. We modify the boundary condition in the PB equation

$$\begin{cases} -\Delta \Psi_\beta + \beta \Phi(\Psi_\beta) = 0 & \text{in } Y_{\mathrm{F}}, \\ \Psi_\beta = \zeta & \text{on } S, \\ \Psi_\beta \text{ is } 1 - \text{periodic.} \end{cases} \tag{104}$$

All unknowns and parameters are exactly the same as the ones in section 3.2.

6.1. The limit case of small β

In the case of constant ζ, we start by studying the behaviour of Ψ_β when β goes to zero. Performing a formal asymptotic expansion

$$\Psi_\beta = \Psi_0 + \beta \Psi_1 + \cdots,$$

it is easy to check that the zero-order term is constant

$$\Psi_0(y) \equiv \zeta,$$

while the first-order term is the solution of the linear problem

$$\begin{cases} -\Delta \Psi_1 = -\Phi(\zeta) & \text{in } Y_{\mathrm{F}}, \\ \Psi_1 = 0 & \text{on } S, \\ \Psi_1 \text{ is } 1 - \text{periodic.} \end{cases} \tag{105}$$

It is not difficult to justify this ansatz and to prove the following error estimate.

Lemma 23. *There exists a positive constant C, independent of β, such that*

$$\|\Psi_\beta - \zeta - \beta \Psi_1\|_{H^1(Y_{\mathrm{F}})} \leqslant C\beta^2.$$

6.2. The limit case of large β: formal asymptotics

We are now interested in the behaviour of Ψ_β for large β. As in section 5.1 we use matching asymptotic expansion. Of course, the outer expansion, being independent of the boundary condition, is the same and we get again (65), namely

$$\Psi_\beta(y) = O\left(\frac{1}{\beta}\right) \qquad \text{away from the boundary } S. \tag{106}$$

To the contrary, the behaviour close to S differs significantly from section 5. We study it locally, in the same geometrical setting as before. We obtain the same differential operator close to the boundary with a different boundary condition

$$-\frac{\partial^2 \Psi_\beta}{\partial q_d^2} + \beta \Phi(\Psi_\beta) + \text{ lower order derivatives in } q_d$$

$$+ \text{ second order differential operator in } q' = 0 \text{ in } Y_{\mathrm{F}} \cap \mathcal{N}(y_0), \tag{107}$$

$$\Psi_\beta = \zeta(q_1, \ldots, q_{d-1}) \text{ on } S \cap \mathcal{N}(y_0). \tag{108}$$

The boundary condition (108) (given ζ potential) is a much stronger constraint than the previous Neumann condition (72). Consequently, we change the inner asymptotic expansion which, instead of (73), is now of the form

$$\Psi_\beta(q', q_d) = \Psi_{0,\zeta}(q', \beta^{1/2} q_d) + \beta^{-1/2} \Psi_{1,\zeta}(q', \beta^{1/2} q_d) + \cdots . \tag{109}$$

Introducing $\xi = \beta^{1/2} q_d$, substituting (109) in (107)–(108) and collecting power-like terms in the resulting equations, we arrive at the following problem for the leading term of the expansion

$$-\frac{d^2}{d\xi^2} \Psi_{0,\zeta}(q', \xi) + \Phi(\Psi_{0,\zeta}(q', \xi)) = 0 \qquad \text{for } \xi > 0, \tag{110}$$

$$\Psi_{0,\zeta}(q', 0) = \zeta(q'). \tag{111}$$

After matching with the outer solution $\Psi_\beta = O(\beta^{-1})$, we impose additionally that $\Psi_{0,\zeta}(q', +\infty) = 0$ and the square integrability of the derivative.

Let $\mathcal{C}(x) = \sum_{j=1}^N n_j^0(\infty) e^{-z_j x}$ be the primitive of $\Phi(x)$. Then the problem (110)–(111) admits the first integral

$$-\frac{1}{2}\left(\frac{d}{d\xi}\Psi_{0,\zeta}\right)^2 + \mathcal{C}(\Psi_{0,\zeta}) = C_1 = \text{ constant.} \tag{112}$$

As we impose $\Psi_{0,\zeta}(q', +\infty) = 0$ and the square integrability of the derivative, it follows that

$$C_1 = \mathcal{C}(0) = \sum_{j=1}^N n_j^0(\infty) > 0. \tag{113}$$

Thus, (111), (112) and (113) give

$$\begin{cases} \Psi_{0,\zeta}|_{\xi=0} = \zeta, \\ \dfrac{d}{d\xi}\Psi_{0,\zeta} = -2\,\mathrm{sign}(\zeta)\sqrt{\mathcal{C}(\Psi_{0,\zeta}) - \mathcal{C}(0)}. \end{cases} \tag{114}$$

Proposition 24. *The Cauchy problem (114) has a unique smooth solution $\Psi_{0,\zeta}$ on $(0, +\infty)$, satisfying (110) and*

$$\begin{aligned} |\Psi_{0,\zeta}(q', \xi)| &\leqslant |\zeta(q')| e^{-\sqrt{C_s}\xi}, \\ \left|\frac{d}{d\xi}\Psi_{0\zeta}(q', \xi)\right| &\leqslant \sqrt{C_0}|\zeta(q')|^{1/2} e^{-\sqrt{C_s}\xi/2}, \end{aligned} \tag{115}$$

where $C_s = \min\{\sum_{j \in j^-} z_j^2 n_j^0(\infty), \sum_{j \in j^+} z_j^2 n_j^0(\infty)\}$ and $C_0 = 2 \max_S |\Phi(\zeta(q'))|$.

Proof. For $\zeta = 0$, the unique solution is $\Psi_{0,\zeta} = 0$ and there is nothing to prove.

For $\zeta \neq 0$, the Cauchy problem (114) has a unique maximal smooth solution on some interval $(0, \ell)$. If $\zeta > 0$, then the solution is positive, monotone decreasing and it reaches the value 0 at $\xi = \ell$. For $\zeta < 0$, it is the opposite situation. But 0 is a critical point of (114) and no trajectory can leave or reach that point. So the solution cannot be zero for some finite ℓ. Therefore, the Cauchy problem (114) has a unique maximal smooth solution on the entire real line $(0, +\infty)$.

Next, a simple calculation gives

$$\left|\frac{d}{d\xi}\Psi_{0,\zeta}(q', \xi)\right|^2 \geqslant C_s |\Psi_{0,\zeta}(q', \xi)|^2,$$

with $C_s = \min\{\sum_{j \in j^-} z_j^2 n_j^0(\infty), \sum_{j \in j^+} z_j^2 n_j^0(\infty)\}$. Consequently, for $\zeta > 0$, we have

$$\frac{\mathrm{d}}{\mathrm{d}\xi} \Psi_{0,\zeta}(q', \xi) \leqslant \zeta(q') \mathrm{e}^{-\sqrt{C_s}\xi}$$

and we establish the exponential decay of $\Psi_{0,\zeta}$ and the first part of (115). For $\zeta < 0$ everything is analogous.

The ordinary differential equation (114) gives

$$\left| \frac{\mathrm{d}}{\mathrm{d}\xi} \Psi_{0,\zeta}(q', \xi) \right|^2 \leqslant 2 \max_S |\Phi(\zeta)| |\Psi_{0,\zeta}(q', \xi)|$$

and we conclude the remaining part of estimate (115). $\qquad\square$

Remark 25. In many situations, for a symmetric electrolyte with ion charges $\pm Q$, the explicit solutions are known. A classical reference is the book [24]. For example, in the case $-z_1 = 1 = z_2$ and $n_1^0(\infty) = n_2^0(\infty) = 1/2$, we have the following Gouy–Chapman solution

$$\Psi_{0,\zeta}(q', \xi) = 2 \ln \frac{1 + \tanh(\zeta/2)\mathrm{e}^{-\xi}}{1 - \tanh(\zeta/2)\mathrm{e}^{-\xi}}.$$

By direct computation we can check that this solution satisfies the properties established in proposition 24. In the general case $\Psi_{0,\zeta}$ can be expressed using elliptic functions. Nevertheless, our simple analysis gave us the properties of the solution without using its explicit form.

6.3. The limit case of large β: rigorous error estimate

We start with the study of the boundary layer function $\Psi_{0,\zeta}$. As in section 5 we use the local change of variables $y \to q$.

Proposition 26. *For each open subset $W_i = Y_F \cap \mathcal{N}(y_i^0)$, let the boundary layer function be defined by*

$$\psi_i^{bl}(q) = \Psi_{0,\zeta}(q', q_d\sqrt{\beta}) \tag{116}$$

for the given boundary data ζ on $S \cap \overline{W}_i$. Then, for any smooth function φ such that $\varphi = 0$ on $\partial q(S \cap \overline{W}_i)$, we have

$$\int_{q(W_i)} K^i \nabla_q \psi_i^{bl}(q) \cdot \nabla_q \varphi \; J^i \, \mathrm{d}q + \beta \int_{q(W_i)} \Phi(\psi_i^{bl}(q)) \varphi J^i \, \mathrm{d}q = \int_{q(W_i)} R_1^i \nabla_{q'} \varphi \; J^i \, \mathrm{d}q$$

$$+ \int_{q(W_i)} R_2^i \varphi \; J^i \, \mathrm{d}q = \int_{q(W_i)} R_3^i \varphi \; J^i \, \mathrm{d}q + \int_{q(\partial W_i \setminus (S \cap \overline{W}_i))} \sigma_1^i \varphi \, \mathrm{d}q', \tag{117}$$

where J^i is the Jacobian of the map $q \to y$, defined by (66), K^i is the metric matrix defined by (67), $\nabla_{q'}$ is gradient with respect to q' and

$$\sqrt{\beta}(\|R_1^i\|_{L^\infty(q(W_i))} + \|\sigma_1^i\|_{L^\infty(q(\partial W_i \setminus (S \cap \overline{W}_i)))}) + \|R_j^i\|_{L^\infty(q(W_i))} \leqslant C\sqrt{\beta}; \tag{118}$$

$$\sqrt{\beta}(\|R_1^i\|_{L^r(q(W_i))} + \|\sigma_1^i\|_{L^\infty(q(\partial W_i \setminus (S \cap \overline{W}_i)))}) + \|R_j^i\|_{L^r(q(W_i))} \leqslant C\beta^{(1-1/r)/2} \qquad j = 2, 3. \tag{119}$$

Proof. By direct calculation, using the estimate (115). We note that the higher derivatives of $\Psi_{0,\zeta}$ with respect to q' satisfy also the estimate (115). $\qquad\square$

Corollary 27. *For all $\varphi \in H^1(W_i)$ such that $\varphi = 0$ on $S \cap \partial W_i$, we have*

$$\int_{W_i} \nabla_y \psi_i^{bl} \cdot \nabla_y \varphi \, dy + \beta \int_{W_i} \Phi(\psi_i^{bl}) \varphi \, dy = \int_{W_i} R_1^i \nabla_y \varphi \, dy$$

$$+ \int_{W_i} R_2^i \varphi \, dy = \int_{W_i} R_3^i \varphi \, dy + \int_{\partial W_i \setminus (S \cap \overline{W}_i)} \sigma_1^i \varphi \, dS, \qquad (120)$$

where redefined remainders σ_1^i, R_j^i, $j = 1, 2, 3$, satisfy (118)–(119).

Using the definition of ψ_i^{bl}, we see that $\psi_i^{bl} = \psi_j^{bl}$ on $W_i \cap W_j$, when $W_i \cap W_j$ is non-empty. Now let $\psi^{bl} = \psi_i^{bl}$ on W_i. As in section 5.2, we make a smooth extension of ψ^{bl} into $Y_F \setminus \overline{Y}_F^\mu$. In $Y_F \setminus \overline{Y}_F^\mu$, ψ^{bl}, together with its derivatives, is exponentially small with respect to $1/\beta$. We simply ignore the exponentially small terms in our estimates. We have:

Proposition 28. *For any $\varphi \in H^1(Y_F)$ such that $\varphi = 0$ on S, we have*

$$\int_{Y_F} \nabla(\Psi_\beta - \psi^{bl}) \cdot \nabla \varphi \, dy + \beta \int_{Y_F} (\Phi(\Psi_\beta) - \Phi(\psi^{bl})) \varphi \, dy = \int_{Y_F} R_\beta^1 \nabla \varphi \, dy$$

$$+ \int_{Y_F} R_\beta^2 \varphi \, dy = \int_{Y_F} R_\beta^3 \varphi \, dy + \sum_{i=1}^{M} \int_{\partial W_i \setminus (S \cap \overline{W}_i)} \sigma_\beta^i \varphi \, dS, \qquad (121)$$

where the global remainders R_β^j, $j = 1, 2, 3$ and σ_β^i, $i = 1, \ldots, M$ satisfy

$$\sqrt{\beta}(\|R_\beta^1\|_{L^r(Y_F)} + \|\sigma_\beta^i\|_{L^r(\partial W_i \setminus (S \cap \overline{W}_i))}) +$$

$$\|R_\beta^j\|_{L^r(Y_F)} \leqslant C\beta^{(1-1/r)/2}, \ \forall r \in [1, +\infty], \ j = 2, 3, \ i = 1, \ldots, M. \qquad (122)$$

Theorem 29. *Let Ψ_β be given by (104) and ψ^{bl} by (116). Then we have the following behaviour for large β:*

$$\|\Psi_\beta - \psi^{bl}\|_{L^1(Y_F)} \leqslant \frac{C}{\beta}, \qquad (123)$$

$$\|\Psi_\beta - \psi^{bl}\|_{L^2(Y_F)} \leqslant \frac{C}{\beta^{1/2}} \qquad (124)$$

$$\|\Psi_\beta - \psi^{bl}\|_{H^1(Y_F)} \leqslant C. \qquad (125)$$

Proof. First we test the variant of (121) involving boundary terms by the regularized sign of $(\Psi_\beta - \psi^{bl})$. After passing to the regularization parameter limit, we get

$$\beta \int_{Y_F} (\Phi(\Psi_\beta) - \Phi(\psi^{bl})) \, \text{sign} \, (\Psi_\beta - \psi^{bl}) \, dy \leqslant C,$$

and after applying a slight generalization of the inequality (79) we get (123).

Next we use the variant of (121) involving only volume terms and test (121) by $g_\beta = \Psi_\beta - \psi^{bl}$. It yields

$$\int_{Y_F} |\nabla(\Psi_\beta - \psi^{bl})|^2 \, dy + \beta \int_{Y_F} (\Phi(\Psi_\beta) - \Phi(\psi^{bl}))(\Psi_\beta - \psi^{bl}) \, dy \leqslant$$

$$C\beta^{1/4} \max_i \|g_\beta\|_{L^2(\partial W_i \cap \mathcal{T})} + C\beta^{1/4} \|g_\beta\|_{L^2(Y_F)}$$

$$\leqslant \frac{\beta \min \Phi'}{2} \|g_\beta\|_{L^2(Y_F)}^2 + \frac{1}{2} \|\nabla g_\beta\|_{L^2(Y_F)}^2 + C. \qquad (126)$$

For $\beta \geqslant \beta_0$, (124)–(125) is a direct consequence of (126). $\qquad \square$

Remark 30. By the same arguments as in section 5, one can obtain, in addition to the inequalities of theorem 29, pointwise estimates for Ψ_β and for the discrepancy $\Psi_\beta - \psi^{bl}$. In the case of the Dirichlet boundary condition these estimates read, for $\beta \geqslant 1$,

$$|\Psi_\beta(y)| \leqslant C_1 \exp\left\{ - C_2 \sqrt{\beta} \operatorname{dist}(y, S) \right\},$$

$$|\nabla \Psi_\beta(y)| \leqslant C_1 \sqrt{\beta} \exp\left\{ - C_2 \sqrt{\beta} \operatorname{dist}(y, S) \right\},$$

$$|\Psi_\beta(y) - \psi^{bl}(y)| \leqslant \frac{C_1}{\sqrt{\beta}} \exp\left\{ - C_2 \sqrt{\beta} \operatorname{dist}(y, S) \right\},$$

where C_1 and C_2 are positive constants, independent of β.

Acknowledgments

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