A SINGULARLY PERTURBED NONLINEAR POISSON–BOLTZMANN EQUATION: UNIFORM AND SUPER-ASYMPTOTIC EXPANSIONS

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Abstract. A steady state Poisson–Nernst–Planck system is investigated, which is conformed into a nonlinear Poisson equation by means of Boltzmann statistics. It describes the electrostatic potential generated by multiple concentrations of ions in a heterogeneous (porous) medium with diluted (solid) particles.

The nonlinear elliptic problem is singularly perturbed with the Debye length as a small parameter related to the electric double layer near the solid particle boundary. For star-shaped solid particles, we prove rigorously that the solution of the problem in spatial dimensions 1d, 2d, and 3d is uniformly and super-asymptotically approximated by a constant reference state.

1. Introduction

We study a steady state Poisson–Nernst–Planck (PNP) system, which describes a multiple ion concentrations coupled with an electrostatic potential in a heterogeneous (porous) medium. It consists of a porous space surrounding diluted solid particles. Our research is motivated in particular by models of Li-Ion batteries, where the porous space is filled with an electrolyte solution. However, such PNP models have numerous applications in describing electro-kinetic phenomena in bio-molecular, electro-chemical and photovoltaic systems.

The considered system of PNP equations is assumed to conform into a Poisson–Boltzmann (PB) equation. This means that the system can be decoupled and reduced to a single nonlinear Poisson equation for the electrostatic field subject to the Boltzmann distribution of the charged particles (i.e. ions) in an electrolyte solution. Concerning derivation and analysis of the respective governing equations see e.g. [1, 5, 22].

The specific mathematical difficulty of the considered PB problem concerns the fact that the resulting nonlinear Poisson equation constitutes a singularly perturbed second order elliptic partial differential equation (PDE) with the Debye length as a small parameter $\lambda \ll 1$. From a physical point

1991 *Mathematics Subject Classification.* 35B25, 35J60, 35Q82, 78A57.

Key words and phrases. Steady State Poisson–Nernst–Planck system, Nonlinear Poisson equation, Boltzmann Statistics, Singular Perturbation, Asymptotic Analysis, Super-asymptotics, Porous media, Electro-chemistry, Photovoltaic.

of view, the Debye length is related to the electric double layer of charges surrounding the surface of the solid particles.

For general methods of asymptotic analysis and its applications to regular and singular perturbations see e.g. [3, 9, 19, 23]. In particular, we refer to [7, 8, 11, 14] for topological methods of asymptotic analysis, and to [10, 26] for boundary layer expansions. Methods of singular perturbations specific to PNP models and PB equations are presented, for example, in [2, 12, 24]. Moreover, we refer to [4, 17] for drift-diffusion (or, generally, to Fokker–Planck) equations in semiconductor physics, which are similar to Nernst–Planck equations for a two-component solution.

Due to the complex multi-scale spatial-temporal behaviour of the PNP system, most previous results in the literature only establish formal asymptotic expansions, typically on two asymptotic scales. Their rigorous justification and proper matching requires highly involved estimates. As the consequence, the macro scales and the micro scales are usually treated separately from one another, which is physically inconsistent.

For the uniform asymptotic approximation valid in both macro and micro scales, the results are available mostly in 1d only. There are very few rigorous analytic results known in this respect in 2d and 3d geometries, see [2].

From the point of view of perturbation theory, singular perturbations of nonlinear equations are challenging problems. We recall, for instance, the following asymptotic techniques to be available. For linear equations, linear asymptotic series can be justified for regularly perturbed problems, while nonlinear Liouville–Green (in particular, the WKB) ansatz is successful for singularly perturbed models. Our situation features a singularly perturbed, nonlinear PDE with small parameter in front of the highest derivative. For such nonlinear singular perturbed PDEs, there is no standard tool of asymptotic analysis available and these problems have to be studied individually.

In this paper, we successfully apply a mixed ansatz to obtain a multiple-scale asymptotic analysis of the steady state PNP equation: a linear asymptotic series for the electrostatic potential and a nonlinear Liouville–Green expansion for the concentrations of charges particles. As result, we obtain a uniform and super-asymptotic approximation. In fact, the solution is constant up to exponential terms $e^{-q/\lambda}$ (for a constant $q > 0$) as $\lambda \searrow 0^+$, which is valid in the bulk region away from the boundary of solid particles.

The main results obtained in the paper are the following ones:

- The uniform and super-asymptotic approximations are proven rigorously in *spatial dimensions* 1d, 2d, and 3d.
- The asymptotic result holds true for *arbitrary star shaped geometries* of particles diluted in a porous space.
- We derive *explicit analytic expressions* of the principal asymptotic terms in terms of exponential functions in 1d and 3d, and in terms of modified Bessel functions of the second kind in 2d.

- The asymptotic expansion takes into account the electric double layer at the particles, which are described by *Robin boundary conditions* for the electrostatic potential.
- The asymptotic expansion is applicable to *multiple particles* with subsequent *averaging* without homogenisation.

Outline of the paper:
In the following Section 2.1, we specify in three subsections first the geometry, secondly the physical model and finally the mathematical model, for which we state first results in Theorem 1. In Section 3, we rigorously perform the asymptotic analysis in the space surrounding one solid particle and state our main Theorem 2. In Section 4, this results is extended to multiple particles.

2. Problem formulation

We start with the description of geometry.

2.1. **Geometry.** Let Ω be a bounded domain in $\mathbb{R}^d$, $d = 1, 2, 3$, with the Lipschitz boundary $\partial\Omega$. We divide Ω into the space ω occupied by a solid particle and the remaining space $\Omega\setminus\overline{\omega}$ corresponding to the porous space surrounding the particle. (In Section 4, we shall consider multiple diluted solid particles.)

We assume ω to be a star shaped domain, which is radially convex with respect to the center $x^0 \in \omega$. Moreover, we associate with ω a local coordinate system centred at x^0 and parameterised by the radial component $r = |x - x^0| \in \mathbb{R}_+$ and the tangential component $\tau \in S_{d-1} \subset \mathbb{R}^{d-1}$. Thus, in 1d, $S_0 = \{-1, 1\}$ is discrete. In 2d, the tangential component τ corresponds to the polar angle and $S_1 = (-\pi, \pi]$. In 3d, the vector $\tau = (\tau_1, \tau_2)$ with $S_2 = [0, \pi] \times (-\pi, \pi]$ is related to spherical coordinates.

Assumption 1. *We assume that the particle boundary $\partial\omega$ can be expressed in the local coordinate system by the positive C^3-function $\theta : \mathbb{R}^{d-1} \mapsto \mathbb{R}_+$ such that $\partial\omega = \{r = \theta(\tau), \tau \in S_{d-1}\}$ and $\mathbb{R}^d\setminus\overline{\omega} = \{r > \theta(\tau), \tau \in S_{d-1}\}$.*

We introduce the Jacobian determinant of the coordinate transformation $x \mapsto (r, \tau)$. On the surface $\partial\omega$ we have the surface element $dS_x = A_{d-1}(\theta(\tau))\, d\tau$, where

$$A_0 = 1, \quad (d\tau = \{-1, 1\} \text{ in 1d}), \qquad A_1(\theta(\tau)) = \left|\tfrac{d}{d\tau} x(\theta(\tau))\right| = \sqrt{\theta^2 + (\theta')^2},$$

and

$$\begin{aligned} A_2(\theta(\tau)) &= \left|\tfrac{\partial}{\partial\tau_1} x(\theta(\tau)) \times \tfrac{\partial}{\partial\tau_2} x(\theta(\tau))\right| \\ &= \theta\sqrt{\theta^2 \sin^2\tau_1 + \theta_{,2}^2 + 2\theta_{,1}(\theta\cos\tau_1)_{,1}\sin^2\tau_1\cos\tau_1}. \end{aligned}$$

For the volume element in $\mathbb{R}^d$, we have $dx = r^{d-1} J_d(\tau)\, dr\, d\tau$ with $J_d = 1$ as $d = 1, 2$ and $J_3(\tau) = \sin\tau_1$ in 3d. Assumption 1 guarantees that $\tau \mapsto A_{d-1}(\theta(\tau)) : \mathbb{R}^{d-1} \mapsto \mathbb{R}_+$ is the twice continuously differentiable function of its parameter $\tau \in S_{d-1}$. This will be used for the asymptotic analysis in performed Section 3.

2.2. **Physical model.** Our considerations are motivated by models of Li-batteries, where solid particles are surrounded by an electrolyte containing multiple species of charge carriers, see [21] and the references therein.

We aim to study the electrostatic potential ϕ and the concentrations of $(n+1)$ components $c = (c_0, \dots, c_n)$, $n \geq 1$ of charged particles (i.e. various ions) in the porous space $\Omega \backslash \overline{\omega}$ (i.e. in the electrolyte surrounding a solid particles in Li-battery models). The physical consistency requires that $c > 0$ (depletion areas as possible in asymptotic analysis of semiconductor pn-junctions are not expected here). The respective electric charges of the ions are denoted by $z_0, \dots, z_n \in \mathbb{R}$ (typical $z_0, \dots, z_n \in \mathbb{Z}$).

On the external boundary $\partial\Omega$ (corresponding to the bath), we assume Dirichlet boundary conditions

$$\phi = \phi^0, \quad c = c^0 \qquad \text{on} \quad \partial\Omega \tag{1}$$

with given a constant $\phi^0 \in \mathbb{R}$ and positive constants $c^0 = (c_0^0, \dots, c_n^0) \in \mathbb{R}_+^{n+1}$. We note that constant Dirichlet data $(\phi^0, c^0 > 0)$ in (1) are needed to guarantee the Boltzmann statistics stated in (15) below. However, this is consistent with the assumptions of the battery models in [21].

The constant Dirichlet data $(\phi^0, c^0 > 0)$ shall also serve as reference values and we require the following two principal assumptions: i) the *charge-neutrality* condition:

$$\sum_{i=0}^{n} z_i c_i^0 = 0, \tag{2}$$

and ii) that there exists a coercivity constant $\underline{K} > 0$ such that for all $\delta \in \mathbb{R}$ the following kind of coercivity statement holds:

$$0 < \underline{K}|\delta|^2 \leq \sum_{i=0}^{n} c_i^0 (-z_i \delta) e^{-z_i \delta}. \tag{3}$$

We remark that due to $c^0 > 0$, a necessary condition for (2) requires that at least two components have opposite charges:

$$\min_{i \in \{0,\dots,n\}} z_i < 0 < \max_{i \in \{0,\dots,n\}} z_i.$$

Moreover, we emphasise that Taylor expansion with respect to $(-z_i\delta)$ proves (3) provided that (2) holds. This can be simplest seen when considering a two component system c_0^0 and c_1^0 with $z_0 = -1$ and $z_1 = 1$ as occurring for instance in semiconductor models. Then, the charge-neutrality condition (2) implies $c_1^0 = c_0^0$ and condition (3) becomes evident since $c_0^0 \delta (e^{\delta} - e^{-\delta}) \geq 2c_0^0 \delta^2$.

We consider the functions ϕ and c rescaled in the dimensionless form. They satisfy the steady state PNP homogeneous equations:

$$-\operatorname{div}\big(D_i(\nabla c_i + z_i c_i \nabla\phi)\big) = 0, \qquad i = 0,\dots,n, \quad \text{in } \Omega\backslash\overline{\omega}, \tag{4}$$

$$-\lambda^2 \operatorname{div}(\varepsilon\nabla\phi) - \tfrac{1}{Z}\sum_{i=0}^{n} z_i c_i = 0, \qquad \text{in } \Omega\backslash\overline{\omega}, \tag{5}$$

where $Z := \sum_{i=0}^{n} z_i^2$ and the parameters $\varepsilon \in \mathbb{R}_+$ and $D_i \in L^\infty(\mathbb{R}^d)$, $D_i > 0$, $i = 0,\dots,n$, are related to a rescaled electric permittivity and positive diffusivities, respectively.

The small parameter $\lambda > 0$ in front of the highest derivative in (5) stands for the Debye length scaled by a characteristic length of the pore space, typically $\lambda \in (10^{-9}, 10^{-2})$, see, for example [1, 5]. Thus, eq. (5) is singularly perturbed with respect to the Debye length.

As boundary conditions on the boundary of the particle $\partial\omega$ with outer unit normal ν, we consider homogeneous Neumann conditions for the fluxes in (4) and an inhomogeneous Robin condition for the electrostatic field ϕ:

$$D_i\big(\tfrac{\partial c_i}{\partial\nu} + z_i c_i \tfrac{\partial\phi}{\partial\nu}\big) = 0, \qquad i = 0,\dots,n, \quad \text{on } \partial\omega, \tag{6}$$

$$\varepsilon\tfrac{\partial\phi}{\partial\nu} = \alpha(\phi - \phi_s), \qquad \text{on } \partial\omega. \tag{7}$$

The condition (7) corresponds to the Gouy–Chapman–Stern model describing a boundary electric double layer (EDL) in terms of a given parameter $\alpha \in \mathbb{R}_+$ and the electrostatic field of the solid particle $\phi_s \in \mathbb{R}$, see e.g. [25].

From a physical point of view, we neglect reactions to occur on $\partial\omega$ by considering a homogeneous Neumann boundary conditions (6) and thus a homogeneous weak formulation (9) below.

2.3. **Mathematical model.** In the following, we denote the solutions of the boundary value problem (1), (4)–(7) with the superscript λ to underline the dependency on the small Debye length λ. Then, a weak solution to (1), (4)–(7) are functions $\phi^\lambda \in H^1(\Omega\backslash\overline{\omega})$ and $c^\lambda = (c_0^\lambda,\dots,c_n^\lambda) \in H^1(\Omega\backslash\overline{\omega})^{n+1} \cap L^\infty(\Omega\backslash\overline{\omega})^{n+1}$ such that $c^\lambda > 0$ satisfies the following weak formulation:

$$\phi^\lambda(x) = \phi^0, \qquad c^\lambda(x) = c^0 \qquad \text{for} \quad x \in \partial\Omega, \tag{8}$$

$$\int_{\Omega\backslash\overline{\omega}} D_i(\nabla c_i^\lambda + z_i c_i^\lambda \nabla\phi^\lambda)\cdot\nabla c_i \, dx = 0, \qquad i = 0,\dots,n,$$
$$\text{for all test-functions } c \in H^1(\Omega\backslash\overline{\omega})^{n+1}\text{: } c = 0 \text{ on } \partial\Omega, \tag{9}$$

$$\int_{\Omega\backslash\overline{\omega}} \big(\varepsilon\nabla\phi^\lambda\cdot\nabla\phi - \tfrac{1}{\lambda^2 Z}\sum_{i=0}^{n} z_i c_i^\lambda \phi\big)\, dx + \int_{\partial\omega} \alpha(\phi^\lambda - \phi_s)\phi \, dS_x = 0,$$
$$\text{for all test-functions } \phi \in H^1(\Omega\backslash\overline{\omega})\text{: } \phi = 0 \text{ on } \partial\Omega. \tag{10}$$

We remark, that the inhomogeneous boundary condition (8) could be reduced to a homogeneous boundary condition in a standard way by introducing $(\phi^\lambda - \phi^0, c^\lambda - c^0)$ as unknowns. However, we prefer to keep the constants (ϕ^0, c^0) in (8), since they represent the zero order asymptotic approximation of the solution $(\phi^\lambda, c^\lambda)$ as $\lambda \searrow 0^+$, which is uniform in $\Omega\backslash\overline{\omega}$ as we shall prove later.

In the following, we will demonstrate that the homogeneous equation (9) allows us to decouple the relations for ϕ^λ from c^λ and reduce the system (8)–(10) by the means of Boltzmann statistics into the single PB equation (17) below. Its solvability is then provided by the assumptions (2) and (3).

We introduce the entropy variables (the chemical potentials)

$$\mu_i^\lambda := \ln c_i^\lambda, \qquad \mu_i^0 := \ln c_i^0, \qquad i = 0, \dots, n. \tag{11}$$

We recall that the chemical potentials could alternatively be defined with respect to the reference state μ^0 as $\ln(c_i^\lambda / c_i^0) = \mu_i^\lambda - \mu_i^0$. Nevertheless, we prefer the notation (11) for the asymptotic reason of $\mu^\lambda \to \mu^0$ as $\lambda \searrow 0^+$ as already discussed above. By using (11), we rewrite (9) in divergence form:

$$\int_{\Omega\backslash\overline{\omega}} D_i c_i^\lambda \nabla(\mu_i^\lambda + z_i \phi^\lambda) \cdot \nabla c_i \, dx = 0, \qquad i = 0, \dots, n. \tag{12}$$

Inserting in (12) the test-functions $c_i = \mu_i^\lambda - \mu_i^0 + z_i(\phi^\lambda - \phi^0)$, we obtain by adding the trivial term $\nabla(\mu^0 + z_i \phi^0) = 0$ (as μ^0 and ϕ^0 are constants)

$$\int_{\Omega\backslash\overline{\omega}} D_i c_i^\lambda \big| \nabla\big(\mu_i^\lambda - \mu_i^0 + z_i(\phi^\lambda - \phi^0)\big)\big|^2 \, dx = 0, \qquad i = 0, \dots, n. \tag{13}$$

Provided $D_i > 0$ and $c_i^\lambda > 0$, it follows from (13) and (8) that

$$\mu_i^\lambda + z_i \phi^\lambda = \mu_i^0 + z_i \phi^0, \qquad i = 0, \dots, n, \tag{14}$$

which implies thermodynamic equilibrium. By combining (14) with (11), we conclude that the concentrations satisfy the Boltzmann statistics:

$$c_i^\lambda = c_i^0 \exp\big(-z_i(\phi^\lambda - \phi^0)\big), \qquad i = 0, \dots, n. \tag{15}$$

Finally, inserting (15) in equation (5) yields the nonlinear Poisson equation

$$-\lambda^2 \mathrm{div}(\varepsilon \nabla \phi^\lambda) - \tfrac{1}{Z} \sum_{i=0}^{n} z_i c_i^0 e^{-z_i(\phi^\lambda - \phi^0)} = 0, \qquad \text{in} \quad \Omega\backslash\overline{\omega}, \tag{16}$$

and together with the Robin boundary condition (7), this turns (10) into the following variational equation:

$$\int_{\Omega\backslash\overline{\omega}} \big(\varepsilon \nabla\phi^\lambda \cdot \nabla\phi - \tfrac{1}{\lambda^2 Z} \sum_{i=0}^{n} z_i c_i^0 e^{-z_i(\phi^\lambda - \phi^0)} \phi\big) \, dx$$
$$+ \int_{\partial\omega} \alpha(\phi^\lambda - \phi_s)\phi \, dS_x = 0 \quad \text{for all} \quad \phi \in H^1(\Omega\backslash\overline{\omega}) : \phi|_{\partial\Omega} = 0. \tag{17}$$

For the unique solvability of (17), see e.g. [2, 5, 16, 17].

From relations (11)–(17), we infer the following existence theorem.

Theorem 1. *For all $\lambda > 0$, there exists the unique weak solution $\phi^\lambda \in H^1(\Omega\backslash\overline{\omega})$, $c^\lambda \in H^1(\Omega\backslash\overline{\omega})^{n+1} \cap L^\infty(\Omega\backslash\overline{\omega})^{n+1}$, $c^\lambda > 0$ of the steady state PNP problem* (8)–(10) *and the entropy variable μ^λ in* (11) *satisfying the following residual estimates*

$$0 < \sum_{i=0}^{n} c_i^\lambda \leq C, \quad |\phi^\lambda - \phi^0| \leq \tfrac{C}{\underline{K}} \sum_{i=0}^{n} |z_i|, \quad \text{with} \quad C := \sum_{i=0}^{n} c_i^0 > 0, \tag{18}$$

$$\begin{aligned}\|\nabla(\phi^\lambda - \phi^0)\|_{L^2(\Omega\backslash\overline{\omega})} + \tfrac{1}{\lambda}\|\phi^\lambda - \phi^0\|_{L^2(\Omega\backslash\overline{\omega})} + \|\phi^\lambda - \phi^0\|_{L^2(\partial\omega)} \\ = \mathrm{O}(\sqrt{\lambda}),\end{aligned} \tag{19}$$

$$\begin{aligned}\|\nabla(\mu^\lambda - \mu^0)\|_{L^2(\Omega\backslash\overline{\omega})^{n+1}} + \tfrac{1}{\lambda}\|\mu^\lambda - \mu^0\|_{L^2(\Omega\backslash\overline{\omega})^{n+1}} + \|\mu^\lambda - \mu^0\|_{L^2(\partial\omega)^{n+1}} \\ = \mathrm{O}(\sqrt{\lambda}),\end{aligned} \tag{20}$$

$$\|c^\lambda - c^0\|_{H^1(\Omega\backslash\overline{\omega})^{n+1}} = \mathrm{O}(\sqrt{\lambda}). \tag{21}$$

Proof. The existence of a unique weak solution to the variational problem (17) follows from general results like [15, 16, 17] thanks to the coercivity of the operator of the problem based on assumption (3).

In the following, we shall derive the residual estimates (18)–(21). In view of (8), we can plug $\phi^\lambda - \phi^0$ as test-function in (17). Hence,

$$\begin{aligned}\int_{\Omega\backslash\overline{\omega}} \Big(\varepsilon\big|\nabla(\phi^\lambda - \phi^0)\big|^2 + \tfrac{1}{\lambda^2 Z}\sum_{i=0}^{n} c_i^0\big(-z_i(\phi^\lambda - \phi^0)\big)e^{-z_i(\phi^\lambda - \phi^0)}\Big)\,dx \\ + \int_{\partial\omega} \alpha(\phi^\lambda - \phi^0)^2\,dS_x = \int_{\partial\omega} \alpha(\phi_s - \phi^0)(\phi^\lambda - \phi^0)\,dS_x\end{aligned}$$

due to $\nabla\phi^0 = 0$. By using the coercivity assumption (3), we obtain

$$\begin{aligned}\int_{\Omega\backslash\overline{\omega}} \big|\nabla(\phi^\lambda - \phi^0)\big|^2\,dx + \tfrac{1}{\lambda^2}\int_{\Omega\backslash\overline{\omega}} (\phi^\lambda - \phi^0)^2\,dx + \int_{\partial\omega} (\phi^\lambda - \phi^0)^2\,dS_x \\ \leq K\Big|\int_{\partial\omega} \alpha(\phi_s - \phi^0)(\phi^\lambda - \phi^0)\,dS_x\Big|.\end{aligned}$$

Here, $K = K(\varepsilon, Z, \underline{K})$ stands for a generic positive constant depending only on ε, Z and the coercivity constant $\underline{K}$ as given in (3).

Next, and applying the trace inequality, see e.g. [2, 15], we continue to estimate

$$\begin{aligned}\int_{\Omega\setminus\overline{\omega}}\big|\nabla(\phi^\lambda-\phi^0)\big|^2\,dx+\tfrac{1}{\lambda^2}\int_{\Omega\setminus\overline{\omega}}(\phi^\lambda-\phi^0)^2\,dx+\int_{\partial\omega}(\phi^\lambda-\phi^0)^2\,dS_x\\ \le K\Big[\lambda^2\int_{\Omega\setminus\overline{\omega}}\big|\nabla(\phi^\lambda-\phi^0)\big|^2\,dx\Big]^{1/4}\Big[\tfrac{1}{\lambda^2}\int_{\Omega\setminus\overline{\omega}}(\phi^\lambda-\phi^0)^2\,dx\Big]^{1/4}\\ \le\frac{3}{4}K^{\frac{4}{3}}\lambda^{2/3}\Big[\int_{\Omega\setminus\overline{\omega}}\big|\nabla(\phi^\lambda-\phi^0)\big|^2\,dx\Big]^{1/3}+\tfrac{1}{4\lambda^2}\int_{\Omega\setminus\overline{\omega}}(\phi^\lambda-\phi^0)^2\,dx,\quad(22)\end{aligned}$$

by Young's inequality and with $K=K(\varepsilon,Z,\underline{K},\alpha,\phi_s,|\partial\omega|)$. Thus,

$$\begin{aligned}\int_{\Omega\setminus\overline{\omega}}\big|\nabla(\phi^\lambda-\phi^0)\big|^2\,dx+\tfrac{3}{4\lambda^2}\int_{\Omega\setminus\overline{\omega}}(\phi^\lambda-\phi^0)^2\,dx+\int_{\partial\omega}(\phi^\lambda-\phi^0)^2\,dS_x\\ \le K^{\frac{4}{3}}\tfrac{3}{4}\lambda^{2/3}\Big[\int_{\Omega\setminus\overline{\omega}}\big|\nabla(\phi^\lambda-\phi^0)\big|^2\,dx\Big]^{1/3},\qquad(23)\end{aligned}$$

which implies

$$\int_{\Omega\setminus\overline{\omega}}\big|\nabla(\phi^\lambda-\phi^0)\big|^2\,dx\le\big(K^{\frac{4}{3}}\tfrac{3}{4}\big)^{3/2}\lambda=\mathrm{O}(\lambda),$$

which in return inserting this into (23) yields (19).

In particular, by iterative differentiation of the Boltzmann statistics in (15), thus $\nabla c_i^\lambda=-z_ic_i^\lambda\nabla\phi^\lambda$ and $\Delta c_i^\lambda=-z_ic_i^\lambda\Delta\phi^\lambda-\nabla(z_ic_i^\lambda)\cdot\nabla\phi^\lambda$ and by using eq. (16), we obtain

$$\Delta c_i^\lambda=\tfrac{1}{\lambda^2Z\varepsilon}z_ic_i^\lambda\sum_{j=0}^n z_jc_j^\lambda-\nabla(z_ic_i^\lambda)\cdot\nabla\phi^\lambda,\qquad i=0,\dots,n,\qquad\text{in }\Omega\setminus\overline{\omega}.$$

Again due to $\nabla\phi^\lambda=-\frac{1}{z_ic_i^\lambda}\nabla c_i^\lambda$ with $c_i^\lambda>0$, summation over i yields

$$\Delta\Big(\sum_{i=0}^n c_i^\lambda\Big)=\tfrac{1}{\lambda^2Z\varepsilon}\Big(\sum_{i=0}^n z_ic_i^\lambda\Big)^2+\sum_{i=0}^n\tfrac{1}{c_i^\lambda}\big|\nabla c_i^\lambda\big|^2\ge 0.$$

Therefore, the function $\sum_{i=0}^n c_i^\lambda$ is subharmonic, and the maximum principle together with the boundary conditions (8) proves the upper bound in the first estimate in (18), which is uniform with respect to the spatial variables and the parameter λ. This implies that $\sup_{i\in\{0,\dots,n\}}c_i^\lambda<C$, and the Cauchy–Schwarz inequality applied to the right-hand side of (3) with $\delta=\phi^\lambda-\phi^0$ leads to the estimate

$$\underline{K}|\phi^\lambda-\phi^0|^2\le-\sum_{i=0}^n z_i(\phi^\lambda-\phi^0)c_i^\lambda<|\phi^\lambda-\phi^0|C\sum_{i=0}^n|z_i|,$$

due to (15). Hence, the second estimate in (18) holds true.

Finally, by using (18), (19) and taking $c=c^\lambda-c^0$ in (9), we have

$$\int_{\Omega\setminus\overline{\omega}}D_i\big|\nabla(c_i^\lambda-c_i^0)\big|^2\,dx=-\int_{\Omega\setminus\overline{\omega}}D_iz_ic_i^\lambda\nabla(\phi^\lambda-\phi^0)\cdot\nabla(c_i^\lambda-c_i^0)\,dx,$$

which yields the estimate (21). This completes the proof. □

In the following section, we construct asymptotic expansions of the solution as $\lambda \searrow 0^+$ and refine the estimates of Theorem 1.

3. Asymptotic expansion

We start by remarking on the zero order approximation, that is when we set $\lambda = 0$. Due to the charge-neutrality assumption (2), the reference state (ϕ^0, c^0) for the steady state PNP problem (8)–(10) is given by the constant Dirichlet conditions (8) given on the external boundary $\partial\Omega$ for the homogeneous equations (9). However, the zero order approximation (ϕ^0, c^0) fails to satisfy the boundary condition (7) on the boundary of the particle $\partial\omega$.

Thus, the challenging task concerns the asymptotic expansion of $(\phi^\lambda - \phi^0, c^\lambda/c^0)$ within a boundary layer near the boundary $\partial\omega$ of the solid particle. This is studied in following section.

3.1. **The principal asymptotic term.** We expect the principal asymptotic term of the singularly perturbed problem (8)–(10) to represent the boundary layer due to the boundary condition (7) on the surface of the solid particle. From a physical point of view, this describes the electric double layer.

The particle boundary $\partial\omega$ can be expressed implicitly as the set $\{r \in \mathbb{R}_+ : r = \theta(\tau)\}$ in the local coordinates (r, τ), see Section 2.1. We represent the near field of $\partial\omega$ by stretching the radial coordinate with the small parameter λ as $\xi = \frac{r-\theta(\tau)}{\lambda}$, $\xi \in \mathbb{R}_+$ and applying the coordinate transformation

$$(r, \tau) \mapsto (\theta(\tau) + \lambda\xi, \tau), \qquad \text{with} \quad \xi = \tfrac{r-\theta(\tau)}{\lambda} \in \mathbb{R}_+$$

to the variational equation (17).

We look for a principal asymptotic term in the expansion of the potential

$$u^\lambda(\xi, \tau) = \frac{1}{\lambda}\Big(\phi^\lambda(\theta + \lambda\xi, \tau) - \phi^0\Big) + \mathrm{o}(1).$$

When asymptotically expanding the nonlinear problem (17) in $\lambda \ll 1$, the o(1)-term comprises the tangential derivatives (that is, $\lambda\nabla_x = \frac{d}{d\xi} + O(\lambda)$), the Neumann to Dirichlet operator at $\partial\omega$, as well as the nonlinear terms in the expansion

$$\sum_{i=0}^{n} z_i c_i^0 e^{-z_i(\phi^\lambda - \phi^0)} = -\sum_{i=0}^{n} z_i^2 c_i^0 (\phi^\lambda - \phi^0) + \mathrm{O}\big((\phi^\lambda - \phi^0)^2\big),$$

for which the zero order sum vanishes due to the charge-neutrality assumption (2).

As the result, the first order principal asymptotic term in (17) leads to the following linearised 1d problem in direction of the radial coordinate: For all $\tau \in S_{d-1}$, we shall find $u^\lambda \in W^{1,2}_{(d-1)/2}(\mathbb{R}_+)$ such that

$$\int_0^\infty \varepsilon\Big(\tfrac{du^\lambda}{d\xi}\tfrac{du}{d\xi} + V u^\lambda u\Big)\big(\theta(\tau)+\lambda\xi\big)^{d-1} J_d(\tau)\, d\xi$$
$$+\,\alpha(\phi^0-\phi_s)(u|_{\xi=0})\, A_{d-1}(\theta(\tau)) = 0 \quad \text{for all} \quad u \in W^{1,2}_{(d-1)/2}(\mathbb{R}_+), \tag{24}$$

which is stated in the properly weighted Sobolev spaces on $\mathbb{R}_+$:

$$W^{1,2}_{(d-1)/2}(\mathbb{R}_+) := \{u : (1+\xi)^{\frac{d-1}{2}} u, (1+\xi)^{\frac{d-1}{2}} \tfrac{du}{d\xi} \in L^2(\mathbb{R}_+)\}.$$

In (24),

$$V := \tfrac{1}{\varepsilon Z}\sum_{i=0}^{n} z_i^2 c_i^0 > 0 \tag{25}$$

and $(\theta+\lambda\xi)^{d-1}J_d$ and A_{d-1} are the Jacobian determinants of the change of variables on the domain in $\mathbb{R}^d$ and at the boundary $\partial\omega$, respectively. We note that in eq. (24), the solution u^λ depends on the tangential coordinate τ only as a parameter through the twice continuously differentiable functions $\theta(\tau)$, $J_d(\tau)$, and $A_{d-1}(\tau)$ as introduced in Section 2.1.

In the following, we establish three auxiliary Lemmata. The first Lemma provides solvability of (24) and describes explicitly its unique solution in terms of exponential functions in 1d and 3d, and in terms of the modified Bessel functions of the second kind $\mathbf{K}_0$ and $\mathbf{K}_1$ in 2d:

Lemma 1. *There exists a unique explicit solution of* (24) *given as*

$$\textit{in 1d}: \quad u^\lambda(\xi) = \frac{\alpha A_0(\phi_s-\phi^0)}{\varepsilon J_1\sqrt{V}}\, e^{-\sqrt{V}\xi}, \tag{26}$$

$$\textit{in 3d}: \quad u^\lambda(\xi,\tau) = \frac{\alpha A_2(\theta(\tau))(\phi_s-\phi^0)}{\varepsilon J_3(\tau)(\theta(\tau)\sqrt{V}+\lambda)(\theta(\tau)+\lambda\xi)}\, e^{-\sqrt{V}\xi}, \tag{27}$$

$$\textit{in 2d}: \quad u^\lambda(\xi,\tau) = \frac{\alpha A_1(\theta(\tau))(\phi_s-\phi^0)\,\mathbf{K}_0\big(\sqrt{V}(\xi+\theta(\tau)/\lambda)\big)}{\varepsilon\theta(\tau)J_2(\tau)\sqrt{V}\,\mathbf{K}_1(\sqrt{V}\theta(\tau)/\lambda)}, \tag{28}$$

where $A_0 = 1$, $A_1(\theta(\tau))$, $A_2(\theta(\tau))$ and $J_0 = J_1 = 1$, $J_2(\tau)$ are defined in Section 2.1 and V is given in (25).

Proof. We rewrite (24) into the following strong formulation as half-space boundary value problem:

$$-\tfrac{d}{d\xi}\big((\theta(\tau)+\lambda\xi)^{d-1}\tfrac{du^\lambda}{d\xi}\big) + V(\theta(\tau)+\lambda\xi)^{d-1}u^\lambda = 0 \quad \text{for } \xi > 0, \tag{29}$$

$$-\,\varepsilon\theta(\tau)^{d-1}J_d(\tau)\tfrac{du^\lambda}{d\xi}(0) + \alpha(\phi^0-\phi_s)A_{d-1}(\theta(\tau)) = 0, \tag{30}$$

$$(1+\xi)^{(d-1)/2}u^\lambda, (1+\xi)^{(d-1)/2}\tfrac{du^\lambda}{d\xi} \to 0 \quad \text{as } \xi \nearrow +\infty. \tag{31}$$

With the decay at infinity according to (31), the general solutions of (29) are: $u^\lambda = K\exp(-\sqrt{V}\xi)$ in 1d, $u^\lambda = K/(\theta(\tau)+\lambda\xi)\exp\big(-\sqrt{V}(\xi+\theta(\tau)/\lambda)\big)$ in 3d, and $u^\lambda = K\,\mathbf{K}_0\big(\sqrt{V}(\xi+\theta(\tau)/\lambda)\big)$ in 2d. The unknown constant

K is determined uniquely from the boundary condition (30), thus inferring the formulas (26)–(28). In 2d, we used the derivative $(\mathbf{K}_0)' = -\mathbf{K}_1$. This completes the proof. □

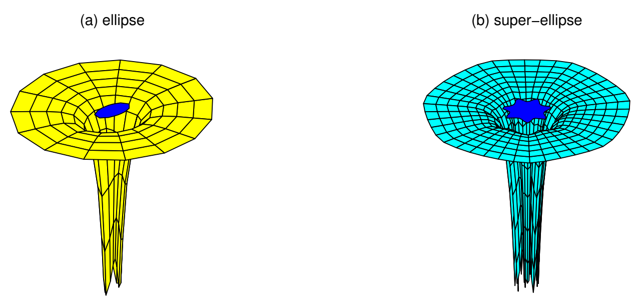

FIGURE 1. Two examples of boundary layers in 2d surrounding a) a ellipsoid particle and b) super-ellipsoid particles

In order to illustrate the boundary layer near the particle surface, Figure 1 depicts in the 2d reference polar coordinates (r, τ) a typical example of the function $x_3 = u^\lambda(\frac{r-\theta(\tau)}{\lambda}, \tau)$ given in (28) in the case $0 > \mathrm{sign}(u^\lambda) = -\mathrm{sign}(\phi_s - \phi^0)$. The domain ω is represented by an ellipse in the plot (a) and by an super-ellipse in the plot (b), which are drawn here in the plane $x_3 = 0$. These pictures show a typical "boundary-layer" behaviour: the angular function $\tau \mapsto u^\lambda(\frac{r-\theta(\,\cdot\,)}{\lambda}, \,\cdot\,)$ is finite at the boundary $\partial\omega$ at the radius $r = \theta(\,\cdot\,)$ and it tends exponentially to zero when increasing the distance to the boundary $r - \theta(\,\cdot\,)$.

The second lemma provides the principal asymptotic term in (26)–(28) as $\lambda \searrow 0^+$ in the stretched and the reference coordinates.

Lemma 2. *The solution of* (24) *obeys the asymptotic behaviour:*

$$u^\lambda(\xi, \tau) = \Big(\frac{\alpha A_{d-1}(\theta(\tau))(\phi_s - \phi^0)}{\varepsilon\theta(\tau)^{d-1} J_d(\tau)\sqrt{V}} + \mathrm{o}(1)\Big) e^{-\sqrt{V}\xi}, \tag{32}$$

and, after the coordinate transformation $r = \theta(\tau) + \lambda\xi$ as

$$\widehat{u}^\lambda(r, \tau) := u^\lambda(\tfrac{r-\theta(\tau)}{\lambda}, \tau) = \Big(\frac{\alpha A_{d-1}(\theta(\tau))(\phi_s - \phi^0)}{\varepsilon\theta(\tau)^{d-1} J_d(\tau)\sqrt{V}} + \mathrm{o}(1)\Big) \times \big(\tfrac{\theta(\tau)}{r}\big)^{\frac{d-1}{2}} e^{-\sqrt{V}\frac{r-\theta(\tau)}{\lambda}}, \tag{33}$$

with respect to $\lambda \searrow 0^+$ in 1d, 2d, and 3d, where $A_0 = 1$, $A_1(\theta(\tau))$, $A_2(\theta(\tau))$ and $J_0 = J_1 = 1$, $J_2(\tau)$ are defined in Section 2.1 and V is given in (25).

Proof. The asymptotic behaviour (32) is a direct consequence of the asymptotic expansions (26)–(28) in small λ. In particular, for (27), we used the following asymptotic formula: $\mathbf{K}_\nu(t) = (1+\mathrm{o}(1))\sqrt{\frac{\pi}{2t}}\exp(-t)$ as $t \nearrow +\infty$ holding for all $\nu \in \mathbb{N}$. Similarly, we obtain (33) after the transformation $r = \theta(\tau) + \lambda\xi$. The proof is complete. $\square$

In the third lemma, on the basis of the transformed boundary layer $\lambda\widehat{u}^\lambda(r,\tau)$ multiplied by λ, we construct an auxiliary function Φ^λ, which solves a nonlinear Poisson equation with the homogeneous Dirichlet condition on $\partial\Omega$:

Lemma 3. *For the solution $u^\lambda(\xi,\tau)$ of problem* (24)*, there exists a function $\Phi^\lambda \in H^1(\Omega\backslash\overline{\omega})$ satisfying*

$$\int_{\Omega\backslash\overline{\omega}} \big(\varepsilon\nabla\Phi^\lambda\cdot\nabla\phi - \tfrac{1}{\lambda^2 Z}\sum_{i=0}^n z_i c_i^0 e^{-z_i\Phi^\lambda}\phi\big)\,dx + \int_{\partial\omega}\alpha(\Phi^\lambda + \phi^0 - \phi_s)\phi\,dS_x$$
$$= \mathrm{Res}(\lambda,\phi) \qquad \text{for all} \quad \phi\in H^1(\Omega\backslash\overline{\omega}), \phi|_{\partial\Omega}=0, \tag{34}$$

$$|\mathrm{Res}(\lambda,\phi)| \le \lambda\big(K + e^{-q/\lambda}\big)\|\phi\|_{H^1(\Omega\backslash\overline{\omega})}, \qquad K>0, \quad q>0, \tag{35}$$

$$\Phi^\lambda(x) = \lambda\big(\widehat{u}^\lambda(r,\tau) + e^{-q/\lambda}U(x)\big), \qquad U\in C^\infty(\overline{\Omega}), \quad q>0, \tag{36}$$

$$\Phi^\lambda = 0, \qquad \text{on} \quad \partial\Omega. \tag{37}$$

$$\Phi^\lambda = \mathrm{O}\big(\lambda e^{-q/\lambda}\big), \qquad \text{away from} \quad \partial\omega, \tag{38}$$

$$\|\nabla\Phi^\lambda\|_{L^2(\Omega\backslash\overline{\omega})} + \tfrac{1}{\lambda}\|\Phi^\lambda\|_{L^2(\Omega\backslash\overline{\omega})} + \|\Phi^\lambda\|_{L^2(\partial\omega)} = \mathrm{O}(\sqrt{\lambda}), \tag{39}$$

where the constants $K>0$ and $q>0$ are specified in the proof and $U\in C^\infty(\overline{\Omega})$ is a smooth lifting function, which is chosen in the proof in order to guarantee (37).

Proof. We start by extending the variational equation (24) from 1d to $\mathbb{R}^d$.

For $\phi\in H^1(\mathbb{R}^d\setminus\overline{\omega})$ supported in Ω, we take $u(\xi,\tau) = \phi(\theta(\tau)+\lambda\xi,\tau)$ as the τ-dependent test-function in (24). Then, after integration over the tangential coordinates $\tau\in S_{d-1}$, we rewrite the result for λu^λ by adding and subtracting as follows:

$$\frac{1}{\lambda}\int_{S_{d-1}}\int_0^\infty \varepsilon\bigg(\frac{\partial(\lambda u^\lambda)}{\partial\xi}\frac{\partial u}{\partial\xi} + \frac{\lambda^2}{(\theta(\tau)+\lambda\xi)^2}\nabla_\tau(\lambda u^\lambda)\cdot\nabla_\tau u$$
$$-\frac{1}{Z}\sum_{i=0}^n z_i c_i^0 e^{-z_i\lambda u^\lambda}(u\bigg)dy + \int_{S_{d-1}}\alpha\Big(\lambda u^\lambda + \phi^0 - \phi_s\Big)(u|_{\xi=0})\,A_{d-1}\,d\tau$$
$$= \lambda\Big(I_1(u) + I_2(u) + I_3(u)\Big), \tag{40}$$

where the tangential gradient is $\nabla_\tau = \frac{\partial}{\partial\tau}$ in 2d and $\nabla_\tau = (\frac{\partial}{\partial\tau_1}, \frac{1}{\sin\tau_1}\frac{\partial}{\partial\tau_2})$ in 3d. Moreover, we denote $dy := \big(\theta(\tau)+\lambda\xi\big)^{d-1}J_d(\tau)\,d\xi\,d\tau$ and the remainder terms I_1, I_2, and I_3 stand for

$$I_1(u) := \int_{S_{d-1}}\int_0^\infty \varepsilon \tfrac{\lambda}{(\theta(\tau)+\lambda\xi)^2}\big(\nabla_\tau u^\lambda \cdot \nabla_\tau u\big)\,dy,$$

$$I_2(u) := -\tfrac{1}{\lambda^2}\int_{S_{d-1}}\int_0^\infty \Big(\varepsilon V\lambda u^\lambda + \tfrac{1}{Z}\sum_{i=0}^n z_i c_i^0 e^{-z_i\lambda u^\lambda}\Big)u\,dy,$$

$$I_3(u) := \int_{S_{d-1}} \alpha u^\lambda (u|_{\xi=0})\,A_{d-1}(\theta(\tau))\,d\tau.$$

The integral I_1 is well defined due to Lemma 1 and Assumption 1. It allows to estimate

$$|I_1(u)| \le K_1 \int_{S_{d-1}}\int_0^\infty \frac{\lambda}{\theta(\tau)+\lambda\xi}|\nabla_\tau u|\,dy, \qquad K_1>0,$$

with $K_1 := \varepsilon\sup_{(\xi,\tau)\in S_{d-1}\times\mathbb{R}_+}\frac{|\nabla_\tau u^\lambda(\xi,\tau)|}{\theta(\tau)+\lambda\xi}$ and $0<K_1<\infty$ due to Lemma 1.

By taking the test-function $u(\xi,\tau)=\phi(\theta+\lambda\xi,\tau)$ and with the change of variables $r=\theta+\lambda\xi$ and $dy\mapsto r^{d-1}J_d\frac{dr}{\lambda}\,d\tau = \frac{1}{\lambda}\,dx$, we obtain for $\widehat{I}_1(\phi) := I_1(u)$

$$|\widehat{I}_1(\phi)| = |I_1(u)| \le K_1\int_{\mathbb{R}^d\setminus\overline{\omega}} |\tfrac{1}{r}\nabla_\tau\phi(x)|\,dx = K_1\int_{\Omega\setminus\overline{\omega}} |\tfrac{1}{r}\nabla_\tau\phi(x)|\,dx \tag{41}$$

since $\phi=0$ outside of Ω. Moreover,

$$\big\|\tfrac{1}{r}\nabla_\tau\phi\big\|_{L^1(\mathbb{R}^d\setminus\overline{\omega})} \le \int_{\Omega\setminus\overline{\omega}}\sqrt{|\tfrac{\partial\phi}{\partial r}|^2 + |\tfrac{1}{r}\nabla_\tau\phi|^2}\,dx = \int_{\Omega\setminus\overline{\omega}}|\nabla\phi|\,dx, \tag{42}$$

where the gradient in (r,τ)-coordinates is assembled by $(\frac{\partial}{\partial r}, \frac{1}{r}\nabla_\tau)$.

Therefore, by using Chauchy-Schwarz, we obtain

$$|\widehat{I}_1(\phi)| \le K_1|\Omega\setminus\overline{\omega}|^{1/2}\sqrt{\int_{\Omega\setminus\overline{\omega}}|\nabla\phi|^2\,dx} \le K_2\|\phi\|_{H^1(\Omega\setminus\overline{\omega})}, \tag{43}$$

with $0<K_2=K_1|\Omega\setminus\overline{\omega}|^{1/2}$.

The integral I_2 can be evaluated with the help of Taylor series

$$\varepsilon V\lambda u^\lambda + \tfrac{1}{Z}\sum_{i=0}^n z_i c_i^0 e^{-z_i\lambda u^\lambda} = \tfrac{1}{Z}\sum_{i=0}^n z_i c_i^0\big(z_i\lambda u^\lambda - 1 + e^{-z_i\lambda u^\lambda}\big) = \mathrm{O}\big((\lambda u^\lambda)^2\big)$$

due to the charge-neutrality condition (2). This implies with the exponential decay of u^λ as $\xi\nearrow+\infty$ as given in (32) the estimate

$$\begin{aligned}|I_2(u)| &\le K_3\int_{S_{d-1}}\int_0^\infty (1+\xi)(u^\lambda)^2\tfrac{|u|}{1+\xi}\,dy \le K_4\int_{S_{d-1}}\int_0^\infty \tfrac{|u|}{1+\xi}\,dy\\ &\le K_5\int_{S_{d-1}}\int_0^\infty \big|\tfrac{\partial u}{\partial\xi}\big|\,dy, \qquad 0<K_3<K_4<K_5,\end{aligned}$$

where the last estimate use a weighted Poincare inequality in $\mathbb{R}_+$, see e.g. [20]. After the change of variables $dy \mapsto \frac{1}{\lambda}\,dx$ and $\frac{\partial u}{\partial \xi} \mapsto \lambda \frac{\partial \psi}{\partial r}$, the transformed integral $\widehat{I}_2$ estimates as

$$|\widehat{I}_2(\phi)| \le K_6 \big\| \tfrac{\partial \phi}{\partial r} \big\|_{L^1(\mathbb{R}^d \setminus \overline{\omega})} \le K_7 \|\phi\|_{H^1(\Omega\setminus\overline{\omega})}, \qquad 0 < K_6 < K_7. \tag{44}$$

Next, since $A_{d-1}(\theta(\tau))\,d\tau \mapsto dS_x$, the integral I_3 transforms into

$$|\widehat{I}_3(\phi)| \le K_8 \|\phi\|_{L^2(\partial\omega)} \le K_9 \|\phi\|_{H^1(\Omega\setminus\overline{\omega})}, \qquad 0 < K_8 < K_9. \tag{45}$$

Applying the coordinate transformation $(\xi, \tau) \mapsto x$ to (40), we conclude for the transformed function $\widehat{u}^\lambda(x) := u^\lambda\big(\frac{r-\theta(\tau)}{\lambda}, \tau\big)$

$$\int_{\Omega\setminus\overline{\omega}} \Big(\varepsilon \nabla(\lambda \widehat{u}^\lambda) \cdot \nabla \phi - \tfrac{1}{\lambda^2 Z} \sum_{i=0}^{n} z_i c_i^0 e^{-z_i \lambda \widehat{u}^\lambda} \phi\Big)\,dx \\ + \int_{\partial\omega} \alpha(\lambda \widehat{u}^\lambda + \phi^0 - \phi_s)\phi\, dS_x = \lambda \operatorname{Res}(\phi), \tag{46}$$

with

$$\operatorname{Res}(\phi) := \widehat{I}_1(\phi) + \widehat{I}_2(\phi) + \widehat{I}_3(\phi),$$

and the residual term at the right hand side estimates from (41)–(45) as

$$|\operatorname{Res}(\phi)| \le K \|\phi\|_{H^1(\Omega\setminus\overline{\omega})}, \qquad K > 0, \tag{47}$$

for a constant $K > 0$.

As $\lambda \searrow 0^+$, it follows from (33) that $\widehat{u}^\lambda \sim e^{-q/\lambda}$ for a constant $q > 0$ satisfying $r - \theta(\tau) \ge q/\sqrt{V} > 0$ in the far field away from the interior boundary $\partial\omega$. This estimate holds, in particular, at the external boundary $\partial\Omega$. Henceforth, adding a smooth lifting function U supported near $\partial\Omega$ and multiplied by $e^{-q/\lambda}$, we can define Φ^λ in (36) such that it fulfils (37) and (38). Then, the relations (46) and (47) stated for $\lambda \widehat{u}^\lambda$ can be rewritten in the form (34) and (35) for Φ^λ. Finally, by applying Theorem 1 to problem (34), we can estimate its solution by (39) according to (19). This completes the proof. □

We emphasise that estimate (38) implies the super-asymptotic approximation of Φ^λ (hence, of $\lambda \widehat{u}^\lambda$) by zero in the bulk region.

3.2. **The first order asymptotic model.** Based on Lemmata 1–3, we formulate the main result of this section, which states the asymptotic model of the singularly perturbed PNP problem (8)–(10):

Theorem 2. *The following uniform estimates hold (and improve* (19)–(21)*):*

$$\|\nabla(\phi^\lambda - \phi^0 - \Phi^\lambda)\|_{L^2(\Omega\setminus\overline{\omega})} + \|\phi^\lambda - \phi^0 - \Phi^\lambda\|_{L^2(\partial\omega)} = \mathrm{O}(\lambda), \tag{48}$$

$$\|\nabla(\mu^\lambda - \mu^0 - M^\lambda)\|_{L^2(\Omega\setminus\overline{\omega})^{n+1}} + \|\mu^\lambda - \mu^0 - M^\lambda\|_{L^2(\partial\omega)^{n+1}} = \mathrm{O}(\lambda), \tag{49}$$

where $C_i^\lambda := \exp(-z_i \Phi^\lambda)$ *and* $M_i^\lambda := \ln C_i^\lambda$, $i = 0, \dots, n$.

Proof. The proof is similar to the proof of Theorem 1. Subtracting (34) from (17) and inserting the test-function $\phi = \phi^\lambda - \phi^0 - \Phi^\lambda$, we get

$$\begin{aligned}\int_{\Omega\setminus\overline{\omega}} \Big(\varepsilon|\nabla(\phi^\lambda - \phi^0 - \Phi^\lambda)|^2 + \tfrac{1}{\lambda^2 Z}\sum_{i=0}^{n} c_i^0\big(-z_i(\phi^\lambda - \phi^0 - \Phi^\lambda)\big)\\ \times\big(e^{-z_i(\phi^\lambda-\phi^0)} - e^{-z_i\Phi^\lambda}\big)\Big)\,dx + \int_{\partial\omega}\alpha(\phi^\lambda - \phi^0 - \Phi^\lambda)^2\,dS_x\\ = -\mathrm{Res}(\lambda, \phi^\lambda - \phi^0 - \Phi^\lambda) \le \lambda K\|\phi^\lambda - \phi^0 - \Phi^\lambda\|_{H^1(\Omega\setminus\overline{\omega})}, \qquad K > 0,\end{aligned}$$

due to Lemma 3. The strict monotonicity of the exponential function yields then (48).

By definition, we have the relation $M_i^\lambda = -z_i\Phi^\lambda$. Subtraction from (14) implies the identity

$$\mu_i^\lambda - \mu_i^0 - M_i^\lambda = -z_i(\phi^\lambda - \phi^0 - \Phi^\lambda), \qquad i = 0,\dots,n. \tag{50}$$

Therefore, from (48) and (50), the relation (49) follows directly. This completes the proof. ☐

For more results concerning L^∞-estimates we refer the reader to [2].

We note that, according to (36) from Lemma 3, the functions Φ^λ, C^λ, and M^λ can be approximated with the help of $\widehat{u}^\lambda$. Therefore, if we set

$$\phi^1 := \phi^0 + \lambda\widehat{u}^\lambda, \qquad c_i^1 := c_i^0 e^{-z_i\lambda\widehat{u}^\lambda}, \qquad \mu_i^1 := \mu_i^0 - z_i\lambda\widehat{u}^\lambda, \tag{51}$$

for $i = 0,\dots,n$, then, from (48) and (49), it follow that

$$\|\phi^\lambda - \phi^1\|_{H^1(\Omega\setminus\overline{\omega})} + \|\mu^\lambda - \mu^1\|_{H^1(\Omega\setminus\overline{\omega})^{n+1}} = \mathrm{O}\big(\lambda(1 + e^{-q/\lambda})\big). \tag{52}$$

Here, we have applied the Trace and Poincare's inequalities. We can further expand $\widehat{u}^\lambda$ with the help of (33) and approximate

$$\phi^1(x) \sim \phi^0 + \lambda\tfrac{\alpha A_{d-1}(\phi_s-\phi^0)}{\varepsilon\theta^{d-1}J_d\sqrt{V}}\big(\tfrac{\theta}{r}\big)^{\frac{d-1}{2}} e^{-\sqrt{V}(|x-x^0|-\theta)/\lambda}, \tag{53}$$

$$c_i^1(x) \sim c_i^0\exp\big(z_i\lambda\tfrac{-\alpha A_{d-1}(\phi_s-\phi^0)}{\varepsilon\theta^{d-1}J_d\sqrt{V}}\big(\tfrac{\theta}{r}\big)^{\frac{d-1}{2}} e^{-\sqrt{V}(|x-x^0|-\theta)/\lambda}\big), \quad i = 0,\dots,n, \tag{54}$$

$$\mu_i^1(x) \sim -z_i\Big(\phi^0 + \lambda\tfrac{\alpha A_{d-1}(\phi_s-\phi^0)}{\varepsilon\theta^{d-1}J_d\sqrt{V}}\big(\tfrac{\theta}{r}\big)^{\frac{d-1}{2}} e^{-\sqrt{V}(|x-x^0|-\theta)/\lambda}\Big), \quad i = 0,\dots,n. \tag{55}$$

We emphasise the following:

- The estimation (52) is uniform with respect to the spatial variable.
- It holds true for all star shaped obstacles $\omega = \{x : |x-x^0| < \theta(\tau), \tau \in S_{d-1}\}$ in the space dimensions $d = 1, 2, 3$.
- Away from $\partial\omega$, the constants (ϕ^0, c^0) and $\mu^0 = \ln c^0$ approximate the solution super-asymptotically.
- In (51), while ϕ^1 and μ^1 present linear asymptotic models, c^1 constitutes a nonlinear approximation of Liouville–Green type.

4. Multiple particles and averaging

Let $\omega_\# = \cup_{j=1}^N \omega^j$ be a union of disjoint particles ω^j, $j = 1, \dots, N$, placed within Ω, thus leaving out the porous space $\Omega \backslash \overline{\omega}_\#$. By $\partial\omega_\#$ we denote the union of boundaries $\cup_{j=1}^N \partial\omega^j$.

We suppose that every domain ω^j is star shaped with respect to a center $x^j \in \omega^j$ and that the boundary $\partial\omega^j$ is described by $\{x : r_j = \theta_j(\tau_j), \tau_j \in S_{d-1}\}$ in the local coordinate system $(r_j = |x - x^j|, \tau_j) \in \mathbb{R}_+ \times S_{d-1}$. Also we assume that ω^j satisfies Assumption 1 and further refer to the respective surface- and volume elements as $A_{d-1}(\theta_j(\tau_j))\, d\tau_j$ and $r_j^{d-1} J_d(\tau_j)\, dr_j\, d\tau_j$ according to the notation introduced in Section 2.1.

Following the lines of Section 2, we treat the problem (8)–(10), where the single particle ω is replaced by the union $\omega_\#$ of particles ω^j, $j = 1, \dots, N$. They are characterised by the physical parameters α_j and $(\phi_s)_j$ in their respective boundary condition (7).

For every ω^j, we define the boundary layer $u_j^\lambda(\xi_i, \tau_j)$ with respect to the stretched variable $\xi_j = (r_j - \theta_j(\tau_j))/\lambda$ analog to the Lemmata 1–3 in Section 3. Since u_j^λ is exponentially small for all $\partial\omega^k$, $k \neq j$, combining the boundary layers yields the following first order asymptotic model (compare to (51)):

$$
\begin{aligned}
\phi^1 &= \phi^0 + \lambda \sum_{j=1}^N \widehat{u}_j^\lambda, \\
c_i^1 &= c_i^0 \exp(-z_i \lambda \sum_{j=1}^N \widehat{u}_j^\lambda), \qquad \text{for} \quad i = 0, \dots, n, \\
\mu_i^1 &= \mu_i^0 - z_i \lambda \sum_{j=1}^N \widehat{u}_j^\lambda, \qquad \text{for} \quad i = 0, \dots, n.
\end{aligned}
\tag{56}
$$

Moreover, the uniform estimation (52) holds in $\Omega \backslash \overline{\omega}_\#$ as well as the super-asymptotic approximation by the constant in the bulk away from $\partial\omega_\#$.

4.1. **Averaging without homogenization.**

For micro-particles, we can average the asymptotic model (56) to a macro-level provided a suitable scaling law for the number N of the solid particles. The explicit asymptotic formula of the solution allows to proceed directly without any homogenisation procedure, see [18].

Let $\Upsilon \subset \mathbb{R}^d$ be a reference cell (typically, the orthotope) and $\omega \subset \Upsilon$. Let the shape of the reference particle $\omega = \{r < \theta(\tau), \tau \in S_{d-1}\}$ be given in the spherical coordinates (r, τ) as introduced in Section 2.1. For a small parameter $\Theta > 0$, let the macro domain Ω be paved with periodic cells Υ^j, $j = 1, \dots, N$, of size Θ, which are homeomorphic to Υ under scaling and translation. Their number N scales as $N = \mathrm{O}(\Theta^{-d}) \nearrow +\infty$ as $\Theta \searrow 0^+$.

We assume that the particles ω^j are distributed uniformly in Ω, namely, $\omega^j \subset \Upsilon^j$ where $\cup_{j=1}^N \omega^j = \omega_\#$. All the particles are assumed to be scaled according to the reference shape ω. In the notation of Section 2.1, $\omega^j = \{r^j < \theta^j(\tau), \tau \in S_{d-1}\}$ in the local spherical coordinates (r^j, τ). Moreover, it is geometrically consistent that $\theta^j(\tau) = \Theta\theta(\tau)$ are proportional to the cell size Θ. Otherwise, if assuming $\theta^j = \mathrm{o}(\Theta)$, then the correction term in (62) below would disappear for $d > 1$.

Based on (56), we suggest a periodic approximation of ϕ^1 written in accordance with expression (53) as

$$\phi^1_\#(r^j, \tau) := \phi^0 + \lambda \tfrac{\alpha A_{d-1}(\Theta\theta(\tau))(\phi_s - \phi^0)}{\varepsilon(\Theta\theta(\tau))^{d-1} J_d(\tau)\sqrt{V}} \big(\tfrac{\Theta\theta(\tau)}{r^j}\big)^{\frac{d-1}{2}} e^{-\sqrt{V}(r^j - \Theta\theta(\tau))/\lambda} \tag{57}$$

for $(r^j, \tau) \in \Upsilon^j \setminus \omega^j$. We note that A_{d-1} is the homogeneous function of degree $d-1$. Furthermore, we transform $\Upsilon^j \mapsto \Upsilon$ by stretching the radial components $r^j = \Theta r$ for $(r, \tau) \in \Upsilon$. As the result we get from (57)

$$\phi^1_\#(\Theta r, \tau) = \phi^0 + \lambda \tfrac{\alpha(\phi_s - \phi^0)}{\varepsilon\sqrt{V}} I(r, \tau) e^{-\Theta\sqrt{V}(r - \theta(\tau))/\lambda} \tag{58}$$

for $(r, \tau) \in \Upsilon \backslash \omega$, with the notation

$$I(r, \tau) := \tfrac{A_{d-1}(\theta(\tau))}{J_d(\tau)} \big(\tfrac{1}{r\theta(\tau)}\big)^{\frac{d-1}{2}}. \tag{59}$$

A standard homogenisation theorem, see e.q. [23, Eq. (4.2), Lemma 4.1, p.57], yields the weak convergence

$$I\big(\tfrac{r^j}{\Theta}, \tau\big) \rightharpoonup \langle I \rangle \quad \text{weakly in } L^2(\Omega) \quad \text{as} \quad \Theta \searrow 0^+ \tag{60}$$

to the averaged (over the cell) value

$$\langle I \rangle := \tfrac{1}{|\Upsilon\backslash\omega|} \int_{\Upsilon\backslash\omega} I(r, \tau) r^{d-1} J_d(\tau)\, dr d\tau. \tag{61}$$

For fixed λ, since $e^{-\Theta\sqrt{V}(r - \theta(\tau))/\lambda} \to 1$ exponentially as $\Theta \searrow 0^+$ and by using (60), we conclude from (58) with the constant averaged model

$$\phi^1_\# \sim \phi^0 + \lambda \tfrac{\alpha(\phi_s - \phi^0)}{\varepsilon\sqrt{V}} \langle I \rangle. \tag{62}$$

The correction term to ϕ^0 in (62) is specified in formulas (59) and (61) for arbitrary star shaped inclusions ω.

The explicit form of averaging is advantageous from the point of view of engineering applications.

5. Conclusion

Considering a singularly perturbed steady state PNP problem (8)–(10), which is conformed by means of the Boltzmann statistics (15) into the quasilinear Poisson equation (17), we rigorously derive a first order asymptotic model (51).

It entails the uniform estimate (52) in the whole porous space, as well as a super-asymptotic approximation by the constant reference state in the bulk region away from a boundary layer near the particles.

Moreover, the analog asymptotic results hold for a porous space surrounding arbitrary many, disjointly diluted solid particles, which have star-shaped geometries in the space dimensions 1d, 2d, and 3d.

For a rigorous homogenization approach to this problem see [6], and [13] for further developments in respect to generalizations to a non-stationary case as well as inhomogeneous boundary fluxes.

Acknowledgments. The research results were obtained with the support of the Austrian Science Fund (FWF) in the framework of the SFB F32 "Mathematical Optimization and Applications in Biomedical Sciences", projects P26147-N26 and P24302. K.F. and V.K. were partially supported by NAWI Graz. V.K. thanks R.Tichy, I.Berkes, and P.Grabner for the kind hospitality at the Graz University of Technology.

References

[1] Allaire G, Brizzi R, Dufreche J-F, Mikelic A, Piatnitski A. Ion transport in porous media: derivation of the macroscopic equations using upscaling and properties of the effective coefficients. *Comput. Geosci.* 2013; **17**: 479–495.

[2] Allaire G, Dufreche J-F, A. Mikelic A, Piatnitski A. Asymptotic analysis of the Poisson-Boltzmann equation describing electrokinetics in porous media. *Nonlinearity* 2013; **26**: 881–910.

[3] Argatov II. *Introduction to Asymptotic Modelling in Mechanics.* Polytechnics: St.-Petersburg; 2004. (in Russian)

[4] Brinkman D, Fellner K, Markowich P, Wolfram M-T. A drift-diffusion-reaction model for excitonic photovoltaic bilayers: asymptotic analysis and a 2-D HDG finite element scheme. *Math. Models Methods Appl. Sci.* 2013; **23**: 83–872.

[5] Burger M, Schlake B, Wolfram M-T. Nonlinear Poisson-Nernst-Planck equations for ion flux through confined geometries. *Nonlinearity* 2012; **25**: 961–990.

[6] Fellner K, Kovtunenko VA. A discontinuous Poisson–Boltzmann equation with interfacial transfer: homogenisation and residual error estimate. *arXiv:***1410.2380** *[math.AP]*; 2014.

[7] Hintermüller M, Kovtunenko VA. From shape variation to topology changes in constrained minimization: a velocity method based concept. *Optim. Methods Softw.* 2011; **26**: 513–532.

[8] Fremiot G, Horn W, Laurain A, Rao M, Sokolowski J. *On the Analysis of Boundary Value Problems in Nonsmooth Domains.* Dissertationes Mathematicae **462**: Inst. Math. Polish Acad. Sci. Warsaw; 2009.

[9] Il'in AM. *Matching of Asymptotic Expansions of Solutions of Boundary Value Problems.* AMS: Providence, RI; 1992.

[10] Kellogg RB, Kopteva N. A singularly perturbed semilinear reaction-diffusion problem in a polygonal domain. *J. Differential Equations* 2010; **248**: 184–208.

[11] Khludnev AM, Kovtunenko VA. *Analysis of Cracks in Solids.* WIT-Press: Southampton, Boston; 2000.

[12] Kosinska ID, Goychuk I, Kostur M, Schmid G, Hänggi P. A singular perturbation approach to the steady-state 1D Poisson-Nernst-Planck modeling. *Acta Physica Polonica B* 2008; **39**: 1137–1160.

[13] Kovtunenko VA. Electro-kinetic structure model with interfacial reactions. in *Proc. 7th ECCOMAS Thematic Conference on Smart Structures and Materials SMART 2015.* Araúo AL, Mota Soares CA, et al. (Eds.): IDMEC; 2015.

[14] Kovtunenko VA, Kunisch K. High precision identification of an object: optimality conditions based concept of imaging. *SIAM J.Control Optim.* 2014; **52**: 773–796.

[15] Ladyzhenskaya OA, Uraltseva NN. *Linear and Quasilinear Elliptic Equations.* Academic Press: New York, London; 1968.

[16] Looker JR. Semilinear elliptic Neumann problems with rapid growth in the nonlinearity. *Bull. Austral. Math. Soc.* 2006; **74**: 161–175.

[17] Markowich PA, Ringhofer CA, Schmeiser Ch. *Semiconductor equations.* Springer-Verlag: Vienna; 1990.

[18] Maz'ya V, Movchan A. Asymptotic treatment of perforated domains without homogenization. *Math. Nachr.* 2010; **283**: 104–125.

[19] Mazja WG, Nasarow SA, Plamenewski BA. *Asymptotische Theorie elliptischer Randwertaufgaben in singulär gestörten Gebieten.* Akademie-Verlag: Berlin; 1991.

[20] Pauly D, Repin S. Functional a posteriori error estimates for elliptic problems in exterior domains. *J. Math. Sci. (N.Y.)* 2009; **162**: 393–406.

[21] Pichler F. *Anwendung der Finite-Elemente Methode auf ein Lithium-Ionen Batterie Modell.* Hochschulschrift: Graz; 2011.

[22] Ray N, Eck Ch, Muntean A, Knabner P. Variable choices of scaling in the homogenization of a Nerst-Planck-Poisson problem. Preprint IAM; **344**: Erlangen; 2011.

[23] Sanchez-Palencia E. *Nonhomogeneous Media and Vibration Theory.* Springer-Verlag: Berlin, New York; 1980.

[24] Singer A, Gillespie D, Norbury J, Eisenberg RS. Singular perturbation analysis of the steady-state Poisson-Nernst-Planck system: applications to ion channels. *European J. Appl. Math.* 2008; **19**: 541–560.

[25] Sprague IB, Dutta P. Depth averaged analytic solution for a laminar flow fuel cell with electric double layer effects. *SIAM J. Appl. Math.* 2012; **72**: 1149–1168.

[26] Vishik MI, Lyusternik LA. Regular degeneration and boundary layer for linear differential equations with small parameter. *Uspehi Mat. Nauk (N.S.)* 1957; **12**: 3–122. (in Russian)

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