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Existence and two-scale convergence of the generalised Poisson–Nernst–Planck problem with non-linear interface conditions

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The paper is devoted to the existence and rigorous homogenisation of the generalised Poisson–Nernst–Planck problem describing the transport of charged species in a two-phase domain. By this, inhomogeneous conditions are supposed at the interface between the pore and solid phases. The solution of the doubly non-linear cross-diffusion model is discontinuous and allows a jump across the phase interface. To prove an averaged problem, the two-scale convergence method over periodic cells is applied and formulated simultaneously in the two phases and at the interface. In the limit, we obtain a non-linear system of equations with averaged matrices of the coefficients, which are based on cell problems due to diffusivity, permittivity and interface electric flux. The first-order corrector due to the inhomogeneous interface condition is derived as the solution to a non-local problem.

Key words: Generalised Poisson–Nernst–Planck model, two-phase interface condition, homogenisation, two-scale convergence

2020 Mathematics Subject Classification: 35B27 (Primary); 35M10; 82C24 (Secondary)

1 Introduction

In this paper, we study a generalised Poisson–Nernst–Planck (PNP) problem formulated in a two-phase domain composed of periodic cells. Non-linear interface conditions are strongly motivated by electro-chemical interfacial reactions, which are of primary importance for electrokinetic applications modelling, for example, electrolyte, Li-Ion batteries and fuel cells. The existence result is stated by means of the fixed point approach. In order to derive an averaged problem with respect to a decreasing cell size, the two-scale convergence method is applied. The PNP problem describes cross-diffusion of multiple charged species, which are expressed in terms of species concentrations and overall electrostatic potential. For the reason of thermodynamic consistency, the concentrations of charged species should satisfy the total mass balance. The consistent generalisation of the multi-component PNP model is made following [14, 18] and the authors themselves [21, 28] based on consideration of the pressure in the mixture with respect to a flow model (Darcy, Stokes).

From a geometric viewpoint, we consider a two-phase space with a microstructure which describes the solid and pores separated by the interface. In the two-phase domain, the field variables are discontinuous since allowing a jump across the interface. For further homogenisation, we will assume that the geometry can be filled periodically with repeating cells and a thin boundary layer complement to the periodic domain. The homogenisation parameter $\varepsilon \in (0, 1)$ describes the size of a periodic cell. The cell consists of the unit solid particle surrounded by the unit pore and separated by an interface.

From the viewpoint of partial differential equations, the parabolic–elliptic equations constituting the PNP system are non-linear, coupled, and differ on the two phases. The double non-linearity appears, first, in the diffusion fluxes and, second, in the interface fluxes. In the classic formulation, the L^∞-estimation of the species concentrations is needed to provide well-posedness of the problem. The solvability of classic PNP systems was studied, for example, in [6, 36] based on the Tikhonov–Schauder fixed point theorem, and in [22] Moser's iteration technique was applied. Following a general approach [36], in the present work, we prove well-posedness of the variational formulation of the generalised PNP problem. The uniform bound is provided by the non-negativity and the total mass balance that hold in the generalised formulation. The *a priori* estimates are obtained involving reasonable assumptions on the diffusivity and permittivity matrices and the boundary fluxes.

For basics of homogenisation techniques, we refer to the two-scale convergence in [1, 33], and to formal two-scale asymptotic expansion in [4, 37, 42]. There is a lot of literature going far beyond linear diffusion, homogeneous Neumann boundary conditions and perforated (one-phase) domains. More complex transport in porous media was considered, for example, in [2, 15, 38]. For an oscillating third boundary condition, we cite [3]. The two-scale convergence was applied to the classic non-linear PNP equations in [24, 34, 39], and to steady-state non-linear Poisson–Boltzmann equations in [16]. Homogenisation of the PNP system in a one-phase perforated domain with the homogeneous Neumann boundary condition and with a jump of the electrical flux was studied in [19]. It is worth remarking that the asymptotic appearance on the one-phase and two-phase domains is different.

In the homogenisation context, very few results are available for inhomogeneous transmission conditions, which are usually assumed to be linear. The works [12, 13] were devoted to the homogenisation of stationary one-component linear diffusion equations in the two-phase domain under linear transmission conditions with a continuous flux. The limit in the linear diffusion system with non-linear transmission conditions was obtained in [20] in the sense of the two-scale convergence. The corrector residual estimates were derived in [29, 35]. In [5], a thermal transfer was considered in a two-phase domain with an imperfect interface, where both the temperature and the flux are discontinuous across the interface. Coupled multi-component reaction-diffusion systems were treated with respect to non-linear reaction terms over the domain in [10] and examined for degenerate asymptotic behaviour in [32] using the two-scale convergence. Finally, in [11], a non-linear transmission condition was treated with respect to the homogenisation procedure with the help of Minty's argument.

In the present paper, we give novel results directed to the following specialties.

- Following [32, 41], we express the two-scale convergence equivalently with the help of a scale transformation. In comparison with conventional approaches, we perform the weak (respectively, strong) two-scale convergences simultaneously over three geometry components: the pore space, the solid phase and the interface.
- The main homogenisation tool for our problem includes compactness principles formulated in the two-scale weak topology in H^1. Namely, depending on available *a priori* estimates, we provide a general principle of the two-scale convergence for a family of interface-discontinuous functions, its gradient, boundary traces and interface jumps, which have different asymptotic orders. For the PNP problem motivated by the described electrokinetic phenomena, its scaling is related to the method of asymptotic homogenisation and results into modified cell problems.
- The principal difficulty of the electrokinetic modelling concerns the interface fluxes due to reactions which cannot depend linearly on the field variables as established in the well-posedness analysis in [26, 27]. Therefore, the suggested inhomogeneous interface conditions are non-linear. Moreover, they do not satisfy any periodicity assumptions since depending on the state variables distributed over the domain. Due to the non-linear interface fluxes, we derive the first-order asymptotic corrector, which is expressed over cells by a non-local problem.
- Based on the two-scale convergence and using the scale transformation between two-phase domains, we rigorously prove a new homogenisation result for the doubly non-linear drift-diffusion system of PNP focusing on the inhomogeneous flux interface conditions. Compared to the other own works [25, 29], we rely on convergences without residual error estimates for the sharp scaling of the interface fluxes with ε.

The paper has the following structure. In Section 2, we formulate the generalised PNP problem and prove the theorem on well-posedness supported by *a priori* estimates for the solution of the inhomogeneous problem. Section 3 is devoted to homogenisation procedure and contains the main result on averaging. The asymptotic technique is adopted for the case of a two-phase domain in Appendix A. The averaged PNP problem is described by the coupled non-linear system of the elliptic–parabolic type. The coefficients in the problem are found as solutions of the cell problems, which are due to periodic permittivity matrix, periodic diffusivity matrices, and due to the periodic electric flux at the interface. The non-periodic interface reactions are small and appear as corrector terms. Considering further scaling issues is addressed in Discussion.

2 Inhomogeneous PNP problem

2.1 Two-phase geometry

Let $Y = (0, 1)^d$, $d = 2, 3$, be a unit cell with the boundary ∂Y. We split it into the two-phase domain $\Pi \cup \omega$ consisting the isolated solid phase $\overline{\omega} \subset Y$ and the complementary pore space $\Pi := Y \setminus \overline{\omega}$, separated by $\partial\omega$. The interface $\partial\omega$ is assumed to be a Lipschitz continuous, closed manifold such that $\partial\omega \cap \partial Y = \emptyset$. We set the unit normal vector ν outward to the particle ω, thus inward to the pore part Π.

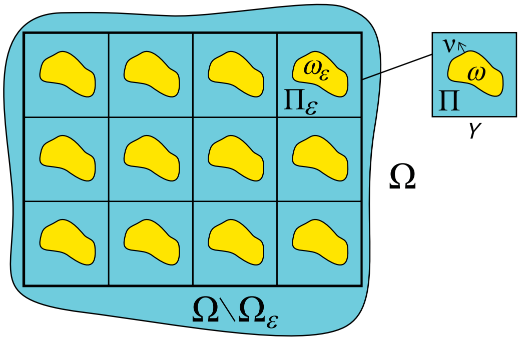

FIGURE 1. A two-phase domain consisting solid particles ω_ε and the pore space Q_ε with the phase interface $\partial\omega_\varepsilon$.

For a small-scale parameter $\varepsilon \in (0, 1)$, every spatial point $x \in \mathbb{R}^d$ can be decomposed

$$x = \varepsilon\left\lfloor \frac{x}{\varepsilon} \right\rfloor + \varepsilon\left\{ \frac{x}{\varepsilon} \right\} \tag{2.1}$$

into the floor part $\lfloor \frac{x}{\varepsilon} \rfloor \in \mathbb{Z}^d$ and the fractional part $\{\frac{x}{\varepsilon}\} \in Y$. There exists a bijection $\mathfrak{C} : \mathbb{Z}^d \mapsto \mathbb{N}$ implying a natural ordering, and its inverse is $\mathfrak{C}^{-1} : \mathbb{N} \mapsto \mathbb{Z}^d$. Based on (2.1), we can determine a local cell Y_ε^l with the index $l = \mathfrak{C}\left(\lfloor \frac{x}{\varepsilon} \rfloor\right)$, such that $x \in Y_\varepsilon^l$, and $\{\frac{x}{\varepsilon}\} \in Y$ are the local coordinates with respect to the cell Y_ε^l.

Let Ω be a domain in $\mathbb{R}^d$ with the Lipschitz continuous boundary $\partial\Omega$ and the unit normal vector ν, which is outward to Ω. Let $I^\varepsilon := \{l \in \mathbb{N} : Y_\varepsilon^l \subset \Omega\}$ be the set of indexes of all periodic cells contained in Ω, and $\Omega_\varepsilon := \mathrm{int}\left(\bigcup_{l\in I^\varepsilon} \overline{Y_\varepsilon^l}\right)$ be the union of these cells. For every index $l \in I^\varepsilon$, after rescaling $y = \{\frac{x}{\varepsilon}\}$, the local coordinate $y \in \omega$ determines the solid particle such that $\{\frac{x}{\varepsilon}\} \in \omega_\varepsilon^l$ with the boundary $\partial\omega_\varepsilon^l$. Its complement composes the pore $\Pi_\varepsilon^l := Y_\varepsilon^l \setminus \overline{\omega_\varepsilon^l}$ by analogy with $\Pi = Y \setminus \overline{\omega}$.

Gathering over all local cells, we define the multi-component disconnected domain of periodic particles (the solid phase) denoted by $\omega_\varepsilon := \bigcup_{l\in I^\varepsilon} \omega_\varepsilon^l$ with the union of boundaries $\partial\omega_\varepsilon := \bigcup_{l\in I^\varepsilon} \partial\omega_\varepsilon^l$. By this transformation, ν remains the unit normal vector to each of $\partial\omega_\varepsilon^l$. The Hausdorff measure $|\partial\omega_\varepsilon|$ of the interface $\partial\omega_\varepsilon$ is of the order $O(\varepsilon^{-1})$ due to $|\partial\omega_\varepsilon^l| = O(\varepsilon^{d-1})$ and the cardinality $|I^\varepsilon| = O(\varepsilon^{-d})$. The periodic domain $\Pi_\varepsilon := \Omega_\varepsilon \setminus \overline{\omega}_\varepsilon$ together with a thin layer $\Omega \setminus \Omega_\varepsilon$, possibly attached to the external boundary $\partial\Omega$, compose the pore space $Q_\varepsilon := (\Omega \setminus \Omega_\varepsilon) \cup \Pi_\varepsilon$, which is a connected, perforated domain. We assume that $|\Omega \setminus \Omega_\varepsilon| = O(\varepsilon)$.

In the homogenisation theory, usually, x refers to as a macro-variable, y as a micro-variable, and (x, y) as the two-scale variables. For fixed $\varepsilon > 0$, the two-phase domain $Q_\varepsilon \cup \omega_\varepsilon$ with the external boundary $\partial\Omega$ and the interface $\partial\omega_\varepsilon$ is illustrated in Figure 1.

Arbitrary functions $u(y) \in H^1(\Pi \cup \omega)$ and $f(x) \in H^1(Q_\varepsilon \cup \omega_\varepsilon)$ given with respect to the micro y and macro x variables allow discontinuity across the interfaces $\partial\omega$ and $\partial\omega_\varepsilon$, respectively. In the unit cell Y, we distinguish the negative face $\partial\omega^-$ as the boundary of the particle ω and the positive face $\partial\omega^+$ as the opposite part of the boundary of the pore Π. Similarly, in each local cell Y_ε^l, we distinguish $(\partial\omega_\varepsilon^l)^-$ and $(\partial\omega_\varepsilon^l)^+$. Gathering over all local cells establishes the positive and negative faces of the interface as $\partial\omega_\varepsilon^\pm = \bigcup_{l\in I^\varepsilon} (\partial\omega_\varepsilon^l)^\pm$. We set the interface jump of u across $\partial\omega$ and of f across $\partial\omega_\varepsilon$ by

$$[\![u]\!]_y := u|_{\partial\omega^+} - u|_{\partial\omega^-}, \quad [\![f]\!] := f|_{\partial\omega_\varepsilon^+} - f|_{\partial\omega_\varepsilon^-}, \tag{2.2}$$

where the corresponding traces of u at $\partial\omega^\pm$ and f at $\partial\omega_\varepsilon^\pm$ are well defined, see [23, Section 1.4].

2.2 Problem formulation

In the two-phase domain $Q_\varepsilon \cup \omega_\varepsilon$, we consider the number $n \geqslant 2$ of charged species with specific charges z_i and unknown concentrations c_i^ε, $i = 1, \dots, n$, together with the overall electrostatic potential φ^ε. They solve the system of Poisson and Nernst–Planck equations for $i = 1, \dots, n$:

$$\frac{\partial c_i^\varepsilon}{\partial t} - \operatorname{div} J_i^\varepsilon = 0, \quad (J_i^\varepsilon)^\top := \sum_{j=1}^n (\nabla c_j^\varepsilon + \varepsilon^\kappa \mathbf{1}_{Q_\varepsilon} \Upsilon_j(\mathbf{c}^\varepsilon) \nabla\varphi^\varepsilon)^\top D_\varepsilon^{ij}, \tag{2.3a}$$

$$-\operatorname{div}\big((\nabla\varphi^\varepsilon)^\top A^\varepsilon\big) = \mathbf{1}_{Q_\varepsilon} \Upsilon_0(\mathbf{c}^\varepsilon) \quad \text{in } Q_\varepsilon \cup \omega_\varepsilon, \tag{2.3b}$$

where the indicator function $\mathbf{1}_{Q_\varepsilon}$ is equal to 1 in Q_ε,and 0 in ω_ε. Here, the Nernst–Planck implies drift–diffusion equations in Q_ε, while linear diffusion together with simple Ohm's law are suggested in ω_ε (see [14, 18, 28] and references therein for the modelling aspects in solid electrolyte). The mixed type non-linear interface conditions are stated on $\partial\omega_\varepsilon$:

$$[\![J_i^\varepsilon]\!]\nu = 0, \quad -J_i^\varepsilon \nu = \varepsilon^{1+\gamma} g_i(\hat{\mathbf{c}}^\varepsilon, \hat{\varphi}^\varepsilon), \tag{2.3c}$$

$$[\![(\nabla\varphi^\varepsilon)^\top A^\varepsilon]\!]\nu = 0, \quad -(\nabla\varphi^\varepsilon)^\top A^\varepsilon \nu + \frac{\alpha}{\varepsilon}[\![\varphi^\varepsilon]\!] = g^\varepsilon, \tag{2.3d}$$

for fixed parameters $\alpha > 0$, $\kappa > 0$, $\gamma \geqslant 0$. The scaling of g_i with ε as $\gamma = 0$ in (2.3c) is natural since it just compensates the interface length $|\partial\omega_\varepsilon| = O(\varepsilon^{-1})$. Then, the uniform *a priori* estimate (see (2.23)) forces conditions $\gamma \geqslant 0$ and $\kappa \geqslant 0$ in the scaling of the non-linearity in (2.3a). Whereas $\kappa > 0$ is assumed for the averaging procedure (see (3.9)). The factor $1/\varepsilon$ in (2.3d) will be explained later in (2.14).

Below we explain the constitutive relations (2.3) in more details.

The non-linear convection terms Υ_0 and $\Upsilon_j, j = 1, \dots, n$, and given by

$$\Upsilon_j(\mathbf{c}) := \frac{C}{k_B \Theta N_A} \frac{c_j^+}{\sum_{k=1}^n c_k^+}\Big(z_j - \frac{1}{C}\Upsilon_0(\mathbf{c})\Big), \quad \Upsilon_0(\mathbf{c}) := C \sum_{j=1}^n z_j \frac{c_j^+}{\sum_{k=1}^n c_k^+}, \tag{2.4}$$

where k_B and N_A are the Boltzmann and Avogadro constants, Θ is the temperature, and the notation $c_k^+ := \max(0, c_k)$ was used. The expressions (2.4) imply a generalisation of the diffusion fluxes J_i^ε that preserves the non-negativity $\mathbf{c}^\varepsilon \geqslant 0$ and the total mass balance $\sum_{k=1}^n c_k^\varepsilon = C > 0$ following the approach of [14, 36].

In (2.3d), the periodic at the interface $\partial\omega_\varepsilon$ function is set $g^\varepsilon(t, x) := (U_\varepsilon g)(t, x) = g\big(t, \{\frac{x}{\varepsilon}\}\big)$. Here, $g \in L^\infty(0, T; L^2(\partial\omega))$ denotes the electric flux through the interface in the unit cell. The family of matrices $A^\varepsilon(x) := (U_\varepsilon A)(x) = A\big(\{\frac{x}{\varepsilon}\}\big)$ in (2.3c) and $D_\varepsilon^{ij}(x) := (U_\varepsilon D^{ij})(x) = D^{ij}\big(\{\frac{x}{\varepsilon}\}\big)$, $i, j = 1, \dots, n$, in (2.3a) is determined in Ω and periodic in Ω_ε. The averaging operator U_ε is introduced in Appendix A.

In the two-phase unit cell $\Pi \cup \omega$, we employ the d-by-d matrix of permittivity A and the two-parameter family of d-by-d diffusivity matrices D^{ij}, $i, j = 1, \dots, n$, which satisfy the following assumptions.

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- $A(y) \in L^\infty(\Pi \cup \omega)^{d\times d}$ is uniformly bounded and symmetric positive definite (spd): there exist $0 < \underline{a} \leqslant \bar{a}$ such that

$$\underline{a}|\xi|^2 \leqslant \xi^\top A(y)\,\xi \leqslant \bar{a}|\xi|^2 \quad \text{for } \xi \in \mathbb{R}^d; \tag{2.5}$$

- $D^{ij}(y) \in L^\infty(\Pi \cup \omega)^{d\times d}$ are uniformly bounded and elliptic: there exist $0 < \underline{d} \leqslant \bar{d}$ such that for $\xi_1, \dots, \xi_n \in \mathbb{R}^d$

$$\underline{d} \textstyle\sum_{i=1}^n |\xi_i|^2 \leqslant \sum_{i,j=1}^n \xi_i^\top D^{ij}(y)\,\xi_j \leqslant \bar{d} \sum_{i=1}^n |\xi_i|^2; \tag{2.6}$$

- there exists a d-by-d spd-matrix $\tilde{D}(y) \in L^\infty(\Pi \cup \omega)^{d\times d}$ such that

$$\textstyle\sum_{i=1}^n D^{ij} = \tilde{D} \quad \text{for } j = 1, \dots, n. \tag{2.7}$$

- as $\varepsilon \to 0$ the asymptotic expansion of the diffusivity matrices holds:

$$D_\varepsilon^{ij} = \delta_{ij}(U_\varepsilon D) + o(1) \quad \text{for } i, j = 1, \dots, n, \tag{2.8}$$

with a bounded spd-matrix $D(y) \in L^\infty(\Pi \cup \omega)^{d\times d}$ satisfying (2.6) like D^{ij}.

In (2.3c), the notation $\hat{\mathbf{c}}^\varepsilon := [\mathbf{c}^\varepsilon|_{\partial\omega_\varepsilon^+}, \mathbf{c}^\varepsilon|_{\partial\omega_\varepsilon^-}]$ and $\hat{\varphi}^\varepsilon := [\varphi^\varepsilon|_{\partial\omega_\varepsilon^+}, \varphi^\varepsilon|_{\partial\omega_\varepsilon^-}]$ stands for the pair of traces at the phase interface $\partial\omega_\varepsilon$. We assume that the functions $(\hat{\mathbf{c}}^\varepsilon, \hat{\varphi}^\varepsilon) \mapsto g_i$, $\mathbb{R}^{2n} \times \mathbb{R}^2 \mapsto \mathbb{R}$, $i = 1, \dots, n$, describing the interface fluxes of species, are strong-to-strong continuous in L^2-topology (e.g., Lipschitz-continuous), and satisfy

$$\text{balance of the mass: } \textstyle\sum_{i=1}^n g_i(\hat{\mathbf{c}}^\varepsilon, \hat{\varphi}^\varepsilon) = 0; \tag{2.9a}$$

$$\text{growth condition } (K_{\mathrm{g}} > 0)\text{: } \varepsilon \textstyle\sum_{i=1}^n \int_{\partial\omega_\varepsilon} |g_i(\hat{\mathbf{c}}^\varepsilon, \hat{\varphi}^\varepsilon)|^2 \, dS_x \leqslant K_{\mathrm{g}}. \tag{2.9b}$$

Motivated by bounded statistics, an example verifying assumptions (2.9) (see [28]) is

$$g_1 = \frac{\prod_{k=1}^2 \max(0, c_k^\varepsilon|_{\partial\omega_\varepsilon^+}) \max(0, c_k^\varepsilon|_{\partial\omega_\varepsilon^-})}{\sum_{k=1}^n \max(0, c_k^\varepsilon|_{\partial\omega_\varepsilon^+})^2 \cdot \sum_{k=1}^n \max(0, c_k^\varepsilon|_{\partial\omega_\varepsilon^-})^2}, \quad g_2 = -g_1, \quad g_i = 0 \quad \text{for } i \geqslant 3.$$

Moreover, it satisfies the positive production rate condition (see [36]):

$$g_i \cdot \min(0, c_i^\varepsilon|_{\partial\omega_\varepsilon^+}) = g_i \cdot \min(0, c_i^\varepsilon|_{\partial\omega_\varepsilon^-}) = 0. \tag{2.9c}$$

By multiplying (2.3a), (2.3b) with smooth test functions and integrating by parts due to (2.3c), (2.3d), we set a variational formulation of the inhomogeneous PNP problem in the two-phase domain. Given final time $T > 0$, find discontinuous over interface functions $\mathbf{c}^\varepsilon(t, x) = (c_1^\varepsilon, \dots, c_n^\varepsilon)$ and $\varphi^\varepsilon(t, x)$ in the trial space

$$\mathcal{W} = [L^\infty(0, T; L^2(Q_\varepsilon \cup \omega_\varepsilon)) \cap L^2(0, T; H^1(Q_\varepsilon \cup \omega_\varepsilon))]^n \times L^\infty(0, T; H^1(Q_\varepsilon \cup \omega_\varepsilon)),$$

satisfying the following variational equations for $i = 1, \dots, n$:

$$\int_0^T \left\{ \left\langle \frac{\partial c_i^\varepsilon}{\partial t}, \bar{c}_i \right\rangle_{Q_\varepsilon \cup \omega_\varepsilon} + \sum_{j=1}^n \int_{Q_\varepsilon \cup \omega_\varepsilon} (\nabla c_j^\varepsilon)^\top D_\varepsilon^{ij} \nabla \bar{c}_i \, dx + \sum_{j=1}^n \int_{Q_\varepsilon} \varepsilon^\kappa \Upsilon_j(\mathbf{c}^\varepsilon)(\nabla\varphi^\varepsilon)^\top D_\varepsilon^{ij} \nabla \bar{c}_i \, dx \right\} dt$$

$$= \int_0^T\!\!\int_{\partial\omega_\varepsilon} \varepsilon^{1+\gamma} g_i(\hat{\mathbf{c}}^\varepsilon, \hat{\varphi}^\varepsilon) [\![\bar{c}_i]\!] \, dS_x \, dt, \tag{2.10a}$$

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$$\int_{Q_\varepsilon \cup \omega_\varepsilon} (\nabla \varphi^\varepsilon)^\top A^\varepsilon \nabla \bar{\varphi}\, dx - \int_{Q_\varepsilon} \Upsilon_0(\mathbf{c}^\varepsilon)\bar{\varphi}\, dx + \int_{\partial\omega_\varepsilon} \frac{\alpha}{\varepsilon} [\![\varphi^\varepsilon]\!] [\![\bar{\varphi}]\!]\, dS_x$$
$$= \int_{\partial\omega_\varepsilon} g^\varepsilon [\![\bar{\varphi}]\!]\, dS_x, \quad t \in (0,T), \tag{2.10b}$$

for all test functions $\bar{\mathbf{c}}(t,x) = (\bar{c}_1, \dots, \bar{c}_n)$ and $\bar{\varphi}(x)$ from the test space

$$\overline{\mathcal{W}} = [H^1(0,T;L^2(Q_\varepsilon \cup \omega_\varepsilon)) \cap L^2(0,T;H^1(Q_\varepsilon \cup \omega_\varepsilon))]^n \times H^1(Q_\varepsilon \cup \omega_\varepsilon)$$

such that $\bar{\mathbf{c}} = \bar{\varphi} = 0$ on $\partial\Omega$. The time derivative in (2.10a) is understood by means of the duality between $H^1(Q_\varepsilon \cup \omega_\varepsilon)$ and $H^1(Q_\varepsilon \cup \omega_\varepsilon)^*$ such that

$$\int_0^T \left\langle \frac{\partial c_i^\varepsilon}{\partial t}, \bar{c}_i \right\rangle_{Q_\varepsilon \cup \omega_\varepsilon} dt := -\int_0^T\!\!\int_{Q_\varepsilon \cup \omega_\varepsilon} c_i^\varepsilon \frac{\partial \bar{c}_i}{\partial t}\, dx\, dt + \int_{Q_\varepsilon \cup \omega_\varepsilon} c_i^\varepsilon \bar{c}_i\, dx \Big|_{t=0}^{T}. \tag{2.11}$$

In fact, since Υ_j and g_i in (2.10a) are uniformly bounded, the terms build a linear and continuous functional and $\frac{\partial c_i^\varepsilon}{\partial t}(t,\cdot) \in H^1(Q_\varepsilon \cup \omega_\varepsilon)^*$.

The system of parabolic (2.10a) and elliptic (2.10b) equations is supported by the standard initial and Dirichlet boundary conditions:

$$c_i^\varepsilon = c_i^{\text{in}} \quad \text{on } Q_\varepsilon \cup \omega_\varepsilon; \quad c_i^\varepsilon = c_i^{\text{D}}, \quad \varphi^\varepsilon = \varphi^{\text{D}} \quad \text{on } (0,T) \times \partial\Omega. \tag{2.12}$$

The given functions $c_i^{\text{D}} \in H^1(0,T;L^2(\Omega)) \cap L^2(0,T;H^1(\Omega))$, $\varphi^{\text{D}} \in H^1(\Omega)$, and $c_i^{\text{in}} \in H^1(\Omega)$ are assumed to satisfy the balance $\sum_{i=1}^n c_i^{\text{D}} = \sum_{i=1}^n c_i^{\text{in}} = C$ of the total mass $C > 0$, the positivity $c_i^{\text{D}} > 0$, $c_i^{\text{in}} > 0$ and the compatibility conditions $c_i^{\text{D}}(0,\cdot) = c_i^{\text{in}}$.

Based on the properties (2.5)–(2.7) and (2.9), we prove well-posedness of the generalised PNP problem (2.10).

2.3 Well-posedness

In the following, we use the trace theorem for functions $f \in H^1(Q_\varepsilon \cup \omega_\varepsilon)$ with $K_0 > 0$:

$$\frac{1}{\varepsilon} \| [\![f]\!] \|^2_{L^2(\partial\omega_\varepsilon)} \leqslant K_0 \Big(\frac{1}{\varepsilon^2} \|f\|^2_{L^2(\Omega_\varepsilon \cup \omega_\varepsilon)} + \|\nabla f\|^2_{L^2(\Omega_\varepsilon \cup \omega_\varepsilon)^d} \Big) \leqslant \frac{K_0}{\varepsilon^2} \|f\|^2_{H^1(\Omega_\varepsilon \cup \omega_\varepsilon)}, \tag{2.13}$$

and the Poincaré inequalities that hold when $f = 0$ on $\partial\Omega$ (see [16]):

$$\int_{Q_\varepsilon} f^2\, dx \leqslant K_{\text{P}} \int_{Q_\varepsilon} |\nabla f|^2\, dx, \quad K_{\text{P}} > 0;$$
$$\int_{Q_\varepsilon \cup \omega_\varepsilon} f^2\, dx \leqslant K_{\text{DP}} \Big\{ \int_{Q_\varepsilon \cup \omega_\varepsilon} |\nabla f|^2\, dx + \frac{1}{\varepsilon} \int_{\partial\omega_\varepsilon} [\![f]\!]^2\, dS_x \Big\}, \quad K_{\text{DP}} > 0. \tag{2.14}$$

It is worth noting that the discontinuous Poincaré inequality (the second line in (2.14)) prescribes the scaling of the interface term in the left-hand side of the Poisson equation (2.10b) and justifies the equivalent to $L^\infty(0,T;H^1(Q_\varepsilon \cup \omega_\varepsilon))$ norm in (2.16b).

Theorem 2.1 (Well-posedness) *A solution* $(\mathbf{c}^\varepsilon, \varphi^\varepsilon) \in \mathcal{W}$ *to the inhomogeneous PNP problem* (2.10) *exists and satisfies the total mass balance*

$$\sum_{i=1}^n c_i^\varepsilon = C \quad \text{in } Q_\varepsilon \cup \omega_\varepsilon. \tag{2.15}$$

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The following a priori estimates hold in the norm of $\mathcal{W}$ with $K_c, K_\phi > 0$:

$$\|\boldsymbol{c}^\varepsilon\|_c^2 := \|\boldsymbol{c}^\varepsilon\|^2_{L^\infty(0,T;L^2(Q_\varepsilon\cup\omega_\varepsilon))^n} + \|\boldsymbol{c}^\varepsilon\|^2_{L^2(0,T;H^1(Q_\varepsilon\cup\omega_\varepsilon))^n} \leqslant K_c, \tag{2.16a}$$

$$\|\varphi^\varepsilon\|_\varphi^2 := \|\nabla\varphi^\varepsilon\|^2_{L^\infty(0,T;L^2(Q_\varepsilon\cup\omega_\varepsilon))^d} + \frac{1}{\varepsilon}\|[\![\varphi^\varepsilon]\!]\|^2_{L^\infty(0,T;L^2(\partial\omega_\varepsilon))} \leqslant K_\phi \tag{2.16b}$$

uniformly in $\varepsilon \in (0, \varepsilon_0)$ *for* $\varepsilon_0 \in (0, 1)$ *sufficiently small.*

Proof To prove the assertion, we apply the Schauder–Tikhonov fixed point theorem [40].

Starting with a smooth initialisation $c_i^{m_0}$, $m_0 \in \mathbb{N}$, for $i = 1, \ldots, n$ such that

$$c_i^{m_0} = c_i^{\mathrm{D}} \quad \text{on } (0, T) \times \partial\Omega, \quad \textstyle\sum_{i=1}^n c_i^{m_0} = C \quad \text{in } (0, T) \times (Q_\varepsilon \cup \omega_\varepsilon),$$

for $m > m_0$, $m \in \mathbb{N}$, we find the solution $(\mathbf{c}^m, \varphi^m) \in \mathcal{W}$, which satisfy the initial and Dirichlet boundary conditions (2.12) and the linearised equations:

$$\begin{aligned}\int_{Q_\varepsilon\cup\omega_\varepsilon} (\nabla\varphi^m)^\top A^\varepsilon \nabla\bar\varphi \, dx + \int_{\partial\omega_\varepsilon} \frac{\alpha}{\varepsilon}[\![\varphi^m]\!][\![\bar\varphi]\!] \, dS_x \\ = \int_{\partial\omega_\varepsilon} g^\varepsilon [\![\bar\varphi]\!] \, dS_x + \int_{Q_\varepsilon} \Upsilon_0(\mathbf{c}^{m-1})\bar\varphi \, dx,\end{aligned} \tag{2.17a}$$

$$\begin{aligned}\int_0^T \left\langle \frac{\partial c_i^m}{\partial t}, \bar c_i \right\rangle_{Q_\varepsilon\cup\omega_\varepsilon} dt + \int_0^T\!\!\int_{Q_\varepsilon\cup\omega_\varepsilon} \sum_{j=1}^n (\nabla c_j^m)^\top D_\varepsilon^{ij} \nabla\bar c_i \, dx\, dt \\ = \int_0^T\!\!\int_{\partial\omega_\varepsilon} \varepsilon^{1+\gamma} g_i^{m-1} [\![\bar c_i]\!] \, dS_x\, dt - \int_0^T\!\!\int_{Q_\varepsilon} \varepsilon^\kappa \sum_{j=1}^n \Upsilon_j(\mathbf{c}^{m-1})(\nabla\varphi^m)^\top D_\varepsilon^{ij} \nabla\bar c_i \, dx\, dt,\end{aligned} \tag{2.17b}$$

for all test functions $(\bar{\mathbf{c}}, \bar\varphi) \in \overline{\mathcal{W}}$ such that $\bar{\mathbf{c}} = \bar\varphi = 0$ on $\partial\Omega$. In (2.17b), the notation $g_i^{m-1} := g_i(\hat{\mathbf{c}}^{m-1}, \hat\varphi^m)$. The iteration $\mathbf{c}^{m-1} \mapsto \varphi^m \mapsto \mathbf{c}^m$ in (2.17) defines the mapping $\mathfrak{M} : \mathcal{W} \mapsto \mathcal{W}$, $(\mathbf{c}^{m-1}, \varphi^m) \mapsto (\mathbf{c}^m, \varphi^{m+1})$. We show that $\mathfrak{M}$ is continuous and has compact image. We start with uniform *a priori* estimates.

Estimation for φ^m. Let us choose in (2.17a) the test function $\bar\varphi = \tilde\varphi^m := \varphi^m - \varphi^{\mathrm{D}}$, which is zero at $(0, T) \times \partial\Omega$ due to the Dirichlet boundary condition, and rearrange the terms using $[\![\varphi^{\mathrm{D}}]\!] = 0$ on $\partial\omega_\varepsilon$ such that:

$$\begin{aligned}I_\varphi^m := \int_{Q_\varepsilon\cup\omega_\varepsilon} (\nabla\tilde\varphi^m)^\top A^\varepsilon \nabla\tilde\varphi^m \, dx + \int_{\partial\omega_\varepsilon} \frac{\alpha}{\varepsilon}[\![\tilde\varphi^m]\!]^2 \, dS_x \\ = \int_{Q_\varepsilon} \Upsilon_0(\mathbf{c}^{m-1})\tilde\varphi^m \, dx - \int_{Q_\varepsilon\cup\omega_\varepsilon} (\nabla\varphi^{\mathrm{D}})^\top A^\varepsilon \nabla\tilde\varphi^m \, dx + \int_{\partial\omega_\varepsilon} g^\varepsilon [\![\tilde\varphi^m]\!] \, dS_x.\end{aligned} \tag{2.18}$$

Applying Young's inequality with a weight $\delta > 0$, we obtain the following upper bounds of the terms in the right-hand side of (2.18). First, estimating from above $\left|\Upsilon_0(\mathbf{c}^{m-1})\right| \leqslant CZ$ in (2.4), where $Z := \sum_{k=1}^n |z_k| > 0$, and using the Poincaré inequality from (2.14), we get

$$\begin{aligned}\left|\int_{Q_\varepsilon} \Upsilon_0(\mathbf{c}^{m-1})\tilde\varphi^m \, dx\right| &\leqslant \frac{\delta K_{\mathrm{P}}}{2} \int_{Q_\varepsilon} |\tilde\varphi^m|^2 \, dx + \frac{(CZ)^2}{2\delta K_{\mathrm{P}}} \int_{Q_\varepsilon} 1 \, dx \\ &\leqslant \frac{\delta}{2}\|\nabla\tilde\varphi^m\|^2_{L^2(Q_\varepsilon)^d} + \frac{K_1}{\delta}, \quad K_1 > 0.\end{aligned}$$

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Second, (2.5) provides the upper bound of A^ε and follows

$$\left|\int_{Q_\varepsilon\cup\omega_\varepsilon}(\nabla\varphi^{\mathrm{D}})^\top A^\varepsilon\nabla\tilde{\varphi}^m\,dx\right|\leqslant\frac{\delta}{2}\|\nabla\tilde{\varphi}^m\|^2_{L^2(Q_\varepsilon\cup\omega_\varepsilon)^d}+\frac{K_2}{\delta},\quad K_2>0.$$

Third, using the uniform boundedness $|g^\varepsilon|\leqslant|g|$ and $|\partial\omega_\varepsilon|=O(\varepsilon^{-1})$, this gets

$$\begin{aligned}\left|\int_{\partial\omega_\varepsilon}g^\varepsilon[\![\tilde{\varphi}^m]\!]\,dS_x\right|&\leqslant\frac{\delta}{\varepsilon}\int_{\partial\omega_\varepsilon}[\![\tilde{\varphi}^m]\!]^2\,dS_x+\frac{\varepsilon}{4\delta}\int_{\partial\omega_\varepsilon}(g^\varepsilon)^2\,dS_x\\&\leqslant\frac{\delta}{\varepsilon}\int_{\partial\omega_\varepsilon}[\![\tilde{\varphi}^m]\!]^2\,dS_x+\frac{K_3}{\delta},\quad K_3>0.\end{aligned}$$

Summarising the three above estimates of the right-hand side of (2.18), we infer the asymptotic relation:

$$I^m_\varphi\leqslant\delta\|\nabla\tilde{\varphi}^m\|^2_{L^2(Q_\varepsilon\cup\omega_\varepsilon)^d}+\frac{\delta}{\varepsilon}\|[\![\tilde{\varphi}^m]\!]\|^2_{L^2(\partial\omega_\varepsilon)}+\frac{K_4}{\delta},\quad K_4>0. \tag{2.19}$$

On the left-hand side of the equation (2.18), using the spd-property of the matrix A^ε in (2.5), the term I^m_φ is estimated from below:

$$\underline{a}\|\nabla\tilde{\varphi}^m\|^2_{L^2(Q_\varepsilon\cup\omega_\varepsilon)^d}+\frac{\alpha}{\varepsilon}\|[\![\tilde{\varphi}^m]\!]\|^2_{L^2(\partial\omega_\varepsilon)}\leqslant I^m_\varphi. \tag{2.20}$$

Gathering together (2.19) and (2.20), for δ chosen sufficiently small such that $\delta<\min\{\underline{a},\alpha\}$, it follows the uniform with respect to ε estimate for all m:

$$\|\nabla\tilde{\varphi}^m\|^2_{L^2(Q_\varepsilon\cup\omega_\varepsilon)^d}+\frac{1}{\varepsilon}\|[\![\tilde{\varphi}^m]\!]\|^2_{L^2(\partial\omega_\varepsilon)}\leqslant K_5,\quad K_5>0. \tag{2.21}$$

Applying to the difference $\tilde{\varphi}^m=\varphi^m-\varphi^{\mathrm{D}}$, the triangle inequality, using $[\![\varphi^{\mathrm{D}}]\!]=0$ on $\partial\omega_\varepsilon$, and taking the supremum over $t\in(0,T)$, from (2.21), it follows the uniform in m and ε estimate:

$$\|\varphi^m\|^2_\varphi\leqslant K_\phi,\quad K_\phi>0, \tag{2.22}$$

with the norm defined in (2.16b).

Estimation for $\mathbf{c}^m$. Let us choose in the equations (2.17b) at $T=\tau$ the test functions $\bar{c}_i=\tilde{c}^m_i:=c^m_i-c^{\mathrm{D}}_i$, which are zero at $(0,T)\times\partial\Omega$, sum them over $i=1,\ldots,n$, and insert the identity $\mathbf{c}^m=\tilde{\mathbf{c}}^m+\mathbf{c}^{\mathrm{D}}$ such that

$$\begin{aligned}I^m_c&:=\sum_{i=1}^n\int_0^\tau\left\{\left\langle\frac{\partial\tilde{c}^m_i}{\partial t},\tilde{c}^m_i\right\rangle_{Q_\varepsilon\cup\omega_\varepsilon}+\sum_{j=1}^n\int_{Q_\varepsilon\cup\omega_\varepsilon}(\nabla\tilde{c}^m_j)^\top D^{ij}_\varepsilon\nabla\tilde{c}^m_i\,dx\right\}dt\\&=\varepsilon^\gamma I^m_1-\varepsilon^\kappa I^m_2-I^m_3-I^m_4,\end{aligned} \tag{2.23}$$

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where the terms in the right-hand side of (2.23) are:

$$I_1^m := \sum_{i=1}^n \int_0^\tau\!\!\int_{\partial\omega_\varepsilon} \varepsilon g_i^{m-1} [\![\tilde{c}_i^m]\!] \, dS_x \, dt,$$

$$I_2^m := \sum_{i,j=1}^n \int_0^\tau\!\!\int_{Q_\varepsilon} \Upsilon_j(\mathbf{c}^{m-1}) \nabla(\varphi^m)^\top D_\varepsilon^{ij} \nabla \tilde{c}_i^m \, dx \, dt,$$

$$I_3^m := \sum_{i=1}^n \int_0^\tau \left\langle \frac{\partial c_i^{\mathrm{D}}}{\partial t}, \tilde{c}_i^m \right\rangle_{Q_\varepsilon \cup \omega_\varepsilon} dt, \quad I_4^m := \sum_{i,j=1}^n \int_0^\tau\!\!\int_{Q_\varepsilon \cup \omega_\varepsilon} (\nabla c_j^D)^\top D_\varepsilon^{ij} \nabla \tilde{c}_i^m \, dx \, dt.$$

We estimate these four integrals using Young's inequality with a weight $\delta > 0$. Applying the trace theorem (2.13) and the growth condition (2.9b), the integral I_1^m is estimated as

$$\begin{aligned} \left| I_1^m \right| &\leqslant \frac{\delta \varepsilon}{4K_0} \int_0^\tau\!\!\int_{\partial\omega_\varepsilon} [\![\tilde{\mathbf{c}}^m]\!]^2 \, dS_x \, dt + \frac{\varepsilon K_0}{\delta} \int_0^\tau\!\!\int_{\partial\omega_\varepsilon} (\mathbf{g}^{m-1})^2 \, dS_x \, dt \\ &\leqslant \frac{\delta}{4} \| \tilde{\mathbf{c}}^m \|^2_{L^2(0,\tau;H^1(Q_\varepsilon\cup\omega_\varepsilon))^n} + \frac{K_1}{\delta}, \quad K_1 > 0, \quad \mathbf{g}^{m-1} = (g_1^{m-1}, \ldots, g_n^{m-1}). \end{aligned}$$

Similarly, using the uniform estimate $\left|\Upsilon_j(\mathbf{c}^{m-1})\right| \leqslant \frac{C}{k_B \Theta N_A}(|z_j| + Z)$, $j = 1, \ldots, n$, in (2.4), the upper bound of D_ε^{ij} from (2.6), the estimate (2.22) of φ^m and the boundedness of $\frac{\partial c_i^{\mathrm{D}}}{\partial t}$ leads in the same manner to the following three asymptotic relations:

$$\left| I_l^m \right| \leqslant \frac{\delta}{4} \| \tilde{\mathbf{c}}^m \|^2_{L^2(0,\tau;H^1(Q_\varepsilon\cup\omega_\varepsilon))^n} + \frac{K_l}{\delta}, \quad K_l > 0, \quad l = 2, 3, 4.$$

Thus, $\left| I_c^m \right|$ in (2.23) is estimated from above as follows with $0 < K_5 = O\left(\frac{1}{\delta}\right)$:

$$\left| I_c^m \right| \leqslant \sum_{l=1}^4 |I_l^m| \leqslant \delta\left(\| \tilde{\mathbf{c}}^m \|^2_{L^2(0,\tau;L^2(Q_\varepsilon\cup\omega_\varepsilon))^n} + \| \nabla \tilde{\mathbf{c}}^m \|^2_{L^2(0,\tau;L^2(Q_\varepsilon\cup\omega_\varepsilon))^{d\times n}} \right) + K_5. \tag{2.24}$$

Due to the compatibility conditions, we have $\tilde{c}_i^m(0) = 0$ and integrate by parts:

$$\int_0^\tau \left\langle \frac{\partial \tilde{c}_i^m}{\partial t}, \tilde{c}_i^m \right\rangle_{Q_\varepsilon \cup \omega_\varepsilon} dt = \frac{1}{2} \int_0^\tau \frac{d}{dt} \int_{Q_\varepsilon \cup \omega_\varepsilon} (\tilde{c}_i^m)^2 \, dx \, dt = \frac{1}{2} \int_{Q_\varepsilon \cup \omega_\varepsilon} (\tilde{c}_i^m(\tau))^2 \, dx.$$

In view of the uniform ellipticity of D_ε^{ij} in (2.6), we estimate I_c^m in (2.23) from below and combine it with the upper bound (2.24) to obtain:

$$\begin{aligned} &\frac{1}{2} \| \tilde{\mathbf{c}}^m(\tau) \|^2_{L^2(Q_\varepsilon\cup\omega_\varepsilon)^n} + (\underline{d} - \delta) \| \nabla \tilde{\mathbf{c}}^m \|^2_{L^2(0,\tau;L^2(Q_\varepsilon\cup\omega_\varepsilon))^{d\times n}} \\ &\qquad \leqslant \delta \int_0^\tau \| \tilde{\mathbf{c}}^m \|^2_{L^2(Q_\varepsilon\cup\omega_\varepsilon)^n} \, dt + K, \quad K > 0. \end{aligned} \tag{2.25}$$

For $\delta < \underline{d}$, applying the Grönwall inequality leads to the estimate $\| \tilde{\mathbf{c}}^m(\tau) \|^2_{L^2(Q_\varepsilon\cup\omega_\varepsilon)^n} \leqslant 2K(1 + 2\delta\tau e^{2\delta\tau})$. Therefore, taking in (2.25) the supremum over $\tau \in (0, T)$, we get

$$\| \tilde{\mathbf{c}}^m \|^2_{L^\infty(0,T;L^2(Q_\varepsilon\cup\omega_\varepsilon))^n} + \| \nabla \tilde{\mathbf{c}}^m \|^2_{L^2(0,T;L^2(Q_\varepsilon\cup\omega_\varepsilon))^{d\times n}} \leqslant K_6, \quad K_6 > 0. \tag{2.26}$$

By the continuous embedding of the spaces $L^\infty \subset L^2$, from (2.26), it follows that $\| \tilde{\mathbf{c}}^m \|^2_{L^2(0,T;L^2(Q_\varepsilon\cup\omega_\varepsilon))^n} \leqslant \text{const}$, hence $\| \tilde{\mathbf{c}}^m \|_c^2 \leqslant \text{const}$ for the norm defined in (2.16a). Inserting $\tilde{\mathbf{c}}^m = \mathbf{c}^m - \mathbf{c}^{\mathrm{D}}$, the triangle inequality provides the uniform in m and ε estimate

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$$\|\mathbf{c}^m\|_c^2 \leqslant K_c, \quad K_c > 0. \tag{2.27}$$

A priori estimates (2.22) and (2.27) are independent on m, henceforth the mapping $\mathfrak{M}$ defined by the iteration (2.17) has the compact image in ball of radius $\sqrt{K_\phi + K_c}$. By the compactness principle, there exists a subsequence still denoted by m such that

$$\varphi^m \rightharpoonup \varphi^\varepsilon, \quad \mathbf{c}^m \rightharpoonup \mathbf{c}^\varepsilon \quad \text{weakly in } \mathcal{W} \quad \text{as } m \to \infty. \tag{2.28}$$

We show that $\mathfrak{M}$ is continuous with respect to the two non-linear terms in (2.17).

The first non-linearity occurs at the interface. Due to the continuous dependence of g_i on $\hat{\mathbf{c}}$ and $\hat{\varphi}$, it holds the limit $g_i^m \to g_i(\hat{\mathbf{c}}^\varepsilon, \hat{\varphi}^\varepsilon)$ provided by the componentwise convergence $\hat{\mathbf{c}}^m \to \hat{\mathbf{c}}^\varepsilon$ and $\hat{\varphi}^m \to \hat{\varphi}^\varepsilon$ in the strong topology of $L^2(\partial\omega_\varepsilon)$ as $m \to \infty$.

The second non-linearity is due to non-linear terms Υ_0 and $(\Upsilon_1, \ldots, \Upsilon_n)$. To prove their continuity, it needs to establish the total mass balance for $\mathbf{c}^m$ and $\mathbf{c}^\varepsilon$. For this task, we sum up the equations (2.17b) over $i = 1, \ldots, n$ skipping the trivial terms $\sum_{j=1}^n \Upsilon_j(\mathbf{c}^m) = 0$ according to (2.4) and $\sum_{i=1}^n g_i^m = 0$ due to the assumption (2.9a). Moreover, $\sum_{i=1}^n D_\varepsilon^{ij} = U_\varepsilon(\sum_{i=1}^n D^{ij}) = U_\varepsilon \tilde{D}$ according to the assumption (2.7), where the averaging operator U_ε is given in Definition A.1. Denoting by $\sigma^m = \sum_{i=1}^n c_i^m - C$ such that $\sigma^m = 0$ as $t = 0$ and $\sigma^m = 0$ on $\partial\Omega$, the substitution into the sum of equations (2.17b) of the test function $\bar{c}_i = \sigma^m$ results in

$$\int_0^T \left\{ \left\langle \frac{\partial \sigma^m}{\partial t}, \sigma^m \right\rangle_{Q_\varepsilon \cup \omega_\varepsilon} + \int_{Q_\varepsilon \cup \omega_\varepsilon} (\nabla \sigma^m)^\top (U_\varepsilon \tilde{D}) \nabla \sigma^m \, dx \right\} dt = 0.$$

We estimate σ^m analogously to (2.25) with $K = 0$, from which it follows $\sigma^m \equiv 0$ and

$$\sum_{i=1}^n c_i^m = C \quad \text{in } Q_\varepsilon \cup \omega_\varepsilon. \tag{2.29}$$

Passing $m \to \infty$ in virtue of (2.28), the total mass balance (2.15) holds for the limit function $\mathbf{c}^\varepsilon$ from (2.28).

For any $\mathbf{c}$ such that $\sum_{k=1}^n c_k = C$, hence $\frac{C}{\sum_{k=1}^n c_k^+} \leqslant 1$, we will show that $\Upsilon_0(\mathbf{c})$ and $\Upsilon_j(\mathbf{c})$, $j = 1, \ldots, n$, are Lipschitz continuous. Due to (2.15) and (2.29), we can take $\mathbf{c}^m$ and $\mathbf{c}^\varepsilon$ from (2.28) as the argument for Υ_0 and estimate the difference:

$$\begin{aligned} |\Upsilon_0(\mathbf{c}^m) - \Upsilon_0(\mathbf{c}^\varepsilon)| &= \left| \frac{C}{\sum_{k=1}^n (c_k^m)^+} \sum_{k=1}^n z_k (c_k^m)^+ - \frac{C}{\sum_{k=1}^n (c_k^\varepsilon)^+} \sum_{k=1}^n z_k (c_k^\varepsilon)^+ \right| \\ &\leqslant (\bar{Z} + Z) \sum_{k=1}^n |(c_k^m)^+ - (c_k^\varepsilon)^+|, \quad \bar{Z} := \max_{k=\{1,\ldots,n\}} |z_k|, \quad Z = \sum_{k=1}^n |z_k|, \end{aligned} \tag{2.30a}$$

by adding and subtracting the same term $\frac{C}{\sum_{k=1}^n (c_k^m)^+} \sum_{k=1}^n z_k (c_k^\varepsilon)^+$. Similarly, for $\Upsilon_j, j = 1, \ldots, n$, we get

$$\begin{aligned} |\Upsilon_j(\mathbf{c}^m) - \Upsilon_j(\mathbf{c}^\varepsilon)| &= \frac{1}{k_B \Theta N_A} \left| C \left(\frac{z_j (c_j^m)^+}{\sum_{k=1}^n (c_k^m)^+} - \frac{z_j (c_j^\varepsilon)^+}{\sum_{k=1}^n (c_k^\varepsilon)^+} \right) - \frac{(c_j^m)^+}{\sum_{k=1}^n (c_k^m)^+} \Upsilon_0(\mathbf{c}^m) \right. \\ &\left. + \frac{(c_j^\varepsilon)^+}{\sum_{k=1}^n (c_k^\varepsilon)^+} \Upsilon_0(\mathbf{c}^\varepsilon) \right| \leqslant \frac{3(\bar{Z} + Z)}{k_B \Theta N_A} \sum_{k=1}^n |(c_k^m)^+ - (c_k^\varepsilon)^+|. \end{aligned} \tag{2.30b}$$

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Therefore, the Lipschitz continuity of Υ_j justifies the limit in the non-linear term in (2.17b). Applying the Cauchy–Schwartz inequality, the convergences (2.28), the compact embedding $H^1(Q_\varepsilon) \hookrightarrow L^2(Q_\varepsilon)$, and the boundedness of Υ_j, it follows that

$$\Big|\int_{Q_\varepsilon} \sum_{j=1}^{n} \big(\Upsilon_j(\mathbf{c}^{m-1})\nabla\varphi^m - \Upsilon_j(\mathbf{c}^\varepsilon)\nabla\varphi^\varepsilon\big)^\top D_\varepsilon^{ij} \nabla \bar{c}_i \, dx\Big|$$

$$\leqslant K\Big(\|(\mathbf{c}^{m-1})^+ - (\mathbf{c}^\varepsilon)^+\|_{L^2(Q_\varepsilon)^n} \|\nabla\varphi^m\|_{L^2(Q_\varepsilon)^d} \|\nabla\bar{c}_i\|_{C^\infty(Q_\varepsilon)^d}$$

$$+ \Big|\int_{Q_\varepsilon} (\nabla\varphi^m - \nabla\varphi^\varepsilon)^\top \nabla\bar{c}_i \, dx\Big|\Big) \to 0 \quad \text{as } m \to 0,$$

with smooth test functions $\bar{c}_i \in C^\infty(Q_\varepsilon)$ and $K > 0$. The limit in Υ_0 in (2.17a) is analogous. Since C^∞-functions are dense in the H^1-space, it follows the continuity of $\mathfrak{M}$.

Henceforth, the existence of a fixed point is provided by the Schauder–Tikhonov theorem. Passing (2.22) and (2.27) to the limit as $m \to \infty$ in virtue of the convergences (2.28) justifies the *a priori* estimates (2.16). □

We note that the non-negativity $\mathbf{c}^\varepsilon \geqslant 0$ under the positive production rate assumption (2.9c) on g_i and for a stronger than (2.7) decoupling assumption $D^{ij} = \delta_{ij}\tilde{D}$ on the diffusivity matrices D^{ij} is proved in [26, 27].

3 Homogenisation procedure

For homogenisation of the PNP problem (2.10), we start with auxiliary cell problems, which are due to periodic matrices of permittivity and diffusivity and periodic electric flux at the interface. A two-scale convergence to an averaged PNP problem is established. After that we proceed with corollaries and state the corrector term due to the non-periodic interface reactions, which refines the two-scale convergence. Respective homogenisation tools that we employ are technical and deduced separately in the Appendix.

3.1 Auxiliary cell problems

Later on we will use the following auxiliary cell problems in the space of periodic through ∂Y, discontinuous across $\partial\omega$ functions

$$H^1_\#(\Pi \cup \omega) := \{u \in H^1(\Pi \cup \omega) : u|_{y_k=0} = u|_{y_k=1},\ k = 1, \ldots, d\},$$

and continuous across the interface functions $H^1_\#(Y) = \{u \in H^1_\#(\Pi \cup \omega) : [\![u]\!]_y = 0\}$.

- The conventional cell problem due to the periodic diffusivity matrix: find a vector-function $N = (N_1, \ldots, N_d)(y) \in (H^1_\#(\Pi \cup \omega))^d$ such that

$$\int_{\Pi\cup\omega} (I + \partial_y N) D \nabla_y u \, dy = 0, \tag{3.1}$$

for all test functions $u \in H^1_\#(\Pi \cup \omega)$. In (3.1), the notation $\partial_y N(y) \in \mathbb{R}^{d\times d}$ for $y \in \Pi \cup \omega$ stands for the matrix of derivatives with entries $(\partial_y N)_{ij} = \frac{\partial N_i}{\partial y_j}$ for $i, j = 1, \dots, d$, and $I \in \mathbb{R}^{d\times d}$ is the identity matrix. A solution of (3.1) exists, and it is defined up to a piecewise constant in $\Pi \cup \omega$, see [42, Chapter 1.2]. Moreover, since the strict inclusion $\overline{\omega} \subset Y$ is assumed, this fact follows that $N = -y$ and $\partial_y N = -I$ in ω.

- The cell problem due to the periodic permittivity matrix: find a vector function $\Phi = (\Phi_1, \dots, \Phi_d)(y) \in (H^1_\#(\Pi \cup \omega))^d$ such that

$$\int_{\Pi\cup\omega} (I + \partial_y \Phi) A \nabla_y u \, dy + \int_{\partial\omega} \alpha [\![\Phi]\!]_y [\![u]\!]_y \, dS_y = 0, \tag{3.2}$$

  for all $u \in H^1_\#(\Pi \cup \omega)$. Compared to (3.1), the integral over the interface $\partial\omega$ appears in (3.2) due to the interface term in (2.10b). Similarly, a solution Φ exists, and it is defined up to a constant in the cell Y.
- The inhomogeneous cell problem due to the periodic electric flux: find $\Lambda(y) \in H^1_\#(\Pi \cup \omega)$ such that

$$\int_{\Pi\cup\omega} (\nabla_y \Lambda)^\top A \, \nabla_y u \, dy + \int_{\partial\omega} \alpha [\![\Lambda]\!]_y [\![u]\!]_y \, dS_y = \int_{\partial\omega} g [\![u]\!]_y \, dS_y, \tag{3.3}$$

  for all test functions $u \in H^1_\#(\Pi \cup \omega)$. Based on the standard elliptic theory for third boundary value problems [30, Chapter 2.5], there exists a solution Λ defined up to a constant value in the cell Y.

3.2 The averaged problem

The main homogenisation result is formulated in the following:

Theorem 3.1 (Averaged problem) *For the inhomogeneous PNP problem* (2.10) *under the asymptotic decoupling assumption* (2.8)*, let the solution* $\boldsymbol{c}^\varepsilon \geqslant 0$ *for* $t \in [0, T]$*. The averaged problem is to find continuous over interface functions*

$$(\boldsymbol{c}^0, \varphi^0)(t, x) \in [L^\infty(0, T; L^2(\Omega) \cap L^2(0, T; H^1(\Omega))]^n \times L^\infty(0, T; H^1(\Omega))$$

satisfying for $i = 1, \dots, n$ *the variational equations*

$$\int_0^T \left\{ \left\langle \frac{\partial c_i^0}{\partial t}, v_i \right\rangle_\Omega + \int_\Omega (\nabla c_i^0)^\top D^0 \nabla v_i \, dx \right\} dt = 0, \tag{3.4a}$$

$$\int_\Omega \left([(\nabla\varphi^0)^\top A^0 + (G^0)^\top] \nabla v - \varkappa \Upsilon_0(\boldsymbol{c}^0) v \right) dx = 0, \quad \varkappa := \frac{|\Pi|}{|Y|}, \tag{3.4b}$$

for all test functions $v_i(t, x) \in H^1(0, T; L^2(\Omega)) \cap L^2(0, T; H^1_0(\Omega))$ *and* $v \in H^1_0(\Omega)$*, where* $\langle \frac{\partial c_i^0}{\partial t}, v_i \rangle_\Omega$ *stands for the duality pairing between* $H^1(\Omega)$ *and* $H^1(\Omega)^*$*, under the boundary and initial conditions:*

$$\boldsymbol{c}^0 = \boldsymbol{c}^{\mathrm{D}}, \quad \varphi^0 = \varphi^{\mathrm{D}} \quad \text{on } \partial\Omega, \quad \boldsymbol{c}^0 = \boldsymbol{c}^{\mathrm{in}} \quad \text{as } t = 0. \tag{3.4c}$$

In (3.4)*,* Υ_0 *is from* (2.4)*, the averaged spd-matrices* D^0*,* A^0 *and the vector* G^0 *are defined below in* (3.24) *and* (3.18)*. The solutions of* (2.10) *and* (3.4) *admit the following two-scale convergences as* $\varepsilon \to 0$*:*

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$$\left(\boldsymbol{c}^{\varepsilon},\varphi^{\varepsilon},\boldsymbol{c}^{\varepsilon}|_{\partial\omega_{\varepsilon}^{\pm}},\varphi^{\varepsilon}|_{\partial\omega_{\varepsilon}^{\pm}},\frac{1}{\varepsilon}[\![\varphi^{\varepsilon}]\!]\right)\xrightarrow{2}\left(\boldsymbol{c}^{0},\varphi^{0},\boldsymbol{c}^{0},\varphi^{0},[\![\Lambda]\!]_y+(\nabla\varphi^{0})^{\top}[\![\Phi]\!]_y\right),\tag{3.5a}$$

$$(\nabla\boldsymbol{c}^{\varepsilon},\nabla\varphi^{\varepsilon})\xrightarrow{2}\left((I+\partial_y N)^{\top}\nabla\boldsymbol{c}^{0},\nabla_y\Lambda+(I+\partial_y\Phi)^{\top}\nabla\varphi^{0}\right)\tag{3.5b}$$

in $L^2\{0,T;[L^2(\Omega)\times L^2(\Pi\cup\omega)]^{n+1}\times[L^2(\Omega)\times L^2(\partial\omega)]^{2n+3}\}$ *for* (3.5a)*, and for* (3.5b) *in* $L^2\{0,T;[L^2(\Omega)\times L^2(\Pi\cup\omega)]^{d\times(n+1)}\}$*. In* (3.5)*,* Φ *and* N *are solutions to the cell problems* (3.2) *and* (3.1)*, and the gradient* $\nabla\boldsymbol{c}=\left(\frac{\partial c_j}{\partial x_i}\right)_{i=1,\dots,d,j=1,\dots,n}$.

It is worth noting that, by the standard variational analysis, from (3.4a) and (3.4b), we derive the strong formulation of the limit diffusion problem in $(0,T)\times\Omega$:

$$\frac{\partial c_i^0}{\partial t}-\operatorname{div}J_i^0=0,\quad (J_i^0)^{\top}:=(\nabla c_i^0)^{\top}D^0,\quad i=1,\dots,n,\tag{3.6a}$$

$$-\operatorname{div}\left((\nabla\varphi^0)^{\top}A^0+(G^0)^{\top}\right)=\varkappa\Upsilon_0(\mathbf{c}^0).\tag{3.6b}$$

Proof For the proof, we apply the homogenisation tools deduced in the Appendix.

Since the *a priori* estimates (2.16) hold for the solution, the cases (ii) and (iii) in Lemma A.5 from Appendix A provide existence of functions

$$\begin{aligned}\varphi^0(t,x)&\in L^{\infty}(0,T;H^1(\Omega)),\quad \varphi^1(t,x,y)\in L^{\infty}(0,T;L^2(\Omega)\times H^1_{\#}(\Pi\cup\omega)),\\ c_i^0(t,x)&\in L^{\infty}(0,T;L^2(\Omega))\cap L^2(0,T;H^1(\Omega)),\\ c_i^1(t,x,y)&\in L^2(0,T;L^2(\Omega)\times H^1_{\#}(\Pi\cup\omega)),\quad i=1,\dots,n,\end{aligned}$$

yielding the two-scale limit according to the convergences (A.12) and (A.14):

$$\left(\mathbf{c}^{\varepsilon},\varphi^{\varepsilon},\mathbf{c}^{\varepsilon}|_{\partial\omega_{\varepsilon}^{\pm}},\varphi^{\varepsilon}|_{\partial\omega_{\varepsilon}^{\pm}},\frac{1}{\varepsilon}[\![\varphi^{\varepsilon}]\!]\right)\xrightarrow{2}\left(\mathbf{c}^{0},\varphi^{0},\mathbf{c}^{0},\varphi^{0},[\![\varphi^1]\!]_y\right),\tag{3.7a}$$

$$(\nabla\mathbf{c}^{\varepsilon},\nabla\varphi^{\varepsilon})\xrightarrow{2}(\nabla\mathbf{c}^0+\nabla_y\mathbf{c}^1,\nabla\varphi^0+\nabla_y\varphi^1)\quad\text{as }\varepsilon\to 0.\tag{3.7b}$$

The case (iiia) of Lemma A.5 ensures the Dirichlet condition following from (2.12):

$$\varphi^0=\varphi^{\mathrm{D}},\quad \mathbf{c}^0=\mathbf{c}^{\mathrm{D}}\quad\text{on }(0,T)\times\partial\Omega.\tag{3.7c}$$

In addition, we will use the auxiliary asymptotic results below. For periodic functions $U_{\varepsilon}g:=g^{\varepsilon}$, since $T_{\varepsilon}g^{\varepsilon}=(T_{\varepsilon}U_{\varepsilon})g=g$ converges to itself in $L^2(\Omega)\times L^2(\partial\omega)$, according to Lemma A.3 of the two-scale convergence this implies:

$$g^{\varepsilon}\xrightarrow{2}g\quad\text{in }L^{\infty}(0,T;L^2(\Omega)\times L^2(\partial\omega)).\tag{3.8}$$

For $\kappa>0$, in the equation (2.10a), we have

$$\int_{Q_{\varepsilon}}\varepsilon^{\kappa}\Upsilon_j(\mathbf{c}^{\varepsilon})(\nabla\varphi^{\varepsilon})^{\top}D_{\varepsilon}^{ij}\nabla\bar{c}_i\,dx=o(1),\quad j=1,\dots,n.\tag{3.9}$$

We apply Lemma A.5 to pass to the limit in the inhomogeneous problem (2.10). First, we consider the equation (2.10b). For arbitrary $v\in H^1_0(\Omega)$ in the domain, we take $\bar{\varphi}=v$ as a test function in (2.10b) such that $[\![v]\!]=0$ on $\partial\omega_{\varepsilon}$ and the boundary terms disappear:

$$\int_{Q_{\varepsilon}\cup\omega_{\varepsilon}}(\nabla\varphi^{\varepsilon})^{\top}A^{\varepsilon}\nabla v\,dx-\int_{Q_{\varepsilon}}\Upsilon_0(\mathbf{c}^{\varepsilon})v\,dx=0.\tag{3.10}$$

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Adding and subtracting $\Upsilon_0(\mathbf{c}^0)$ yield the decomposition

$$\int_{Q_\varepsilon} \Upsilon_0(\mathbf{c}^\varepsilon) v\, dx = \int_{Q_\varepsilon} \Upsilon_0(\mathbf{c}^0) v\, dx + \int_{Q_\varepsilon} (\Upsilon_0(\mathbf{c}^\varepsilon) - \Upsilon_0(\mathbf{c}^0)) v\, dx. \tag{3.11}$$

Since $\Upsilon_0(\mathbf{c}^0) v \in H_0^1(\Omega)$, its integral over the pore part Q_ε can be rewritten over Ω with the help of the asymptotic formula from [16, Lemma 2]:

$$\int_{Q_\varepsilon} \Upsilon_0(\mathbf{c}^0) v\, dx = \varkappa \int_{\Omega} \Upsilon_0(\mathbf{c}^0) v\, dx + O(\varepsilon), \quad \varkappa = \frac{|\Pi|}{|Y|}.$$

Provided by the total mass balance (2.15) and the non-negativity assumption $\mathbf{c}^\varepsilon \geqslant 0$, the function $\mathbf{c}^\varepsilon \mapsto \Upsilon_0$ in (2.4) is linear. Henceforth, from the composition rule (A.3c) of the unfolding operator T_ε (see Definition A.1) implying $T_\varepsilon \Upsilon_0(\mathbf{c}^\varepsilon) = \Upsilon_0(T_\varepsilon \mathbf{c}^\varepsilon)$ and the convergence (3.7), it follows

$$\Upsilon_0(\mathbf{c}^\varepsilon) \overset{2}{\rightharpoonup} \Upsilon_0(\mathbf{c}^0) \quad \text{in } L^2(0, T; L^2(\Omega) \times L^2(\Pi \cup \omega)), \tag{3.12}$$

and together with (3.11),

$$\int_{Q_\varepsilon} \Upsilon_0(\mathbf{c}^\varepsilon) v\, dx \to \frac{\varkappa}{|Y|} \int_{\Omega} \int_{\Pi \cup \omega} \Upsilon_0(\mathbf{c}^0) v\, dx\, dy.$$

Since $T_\varepsilon A^\varepsilon = A$ in Ω_ε due to the periodicity of A as stated in (A.3b) and $|\Omega \setminus \Omega_\varepsilon| \to 0$, based on cases (ib) and (iiib) in Lemma A.4 with $q = v$, we get the limit in (3.10):

$$\frac{1}{|Y|} \int_{\Omega} \int_{\Pi \cup \omega} \left((\nabla \varphi^0 + \nabla_y \varphi^1)^\top A \nabla v - \varkappa \Upsilon_0(\mathbf{c}^0) v \right) dy\, dx = 0. \tag{3.13}$$

In order to represent φ^1 in (3.13), we employ the cell problems (3.2) and (3.3) as follows. For arbitrary $w(y) \in H_\#^1(\Pi \cup \omega)$ in the cell, we can take in (2.10b) another test function $\bar{\varphi} = \varepsilon \eta_{\Omega_\varepsilon} U_\varepsilon w$ with a cut-off function $\eta_{\Omega_\varepsilon}$ supported in Ω_ε and equals one outside an ε-neighborhood of $\partial \Omega_\varepsilon$ (see [4, Chapter 1, Section 5]). Indeed, the periodicity of w on ∂Y guarantees continuity of $U_\varepsilon \bar{\varphi}$ across the local cells, then (2.10b) turns into

$$\begin{aligned} &\int_{Q_\varepsilon \cup \omega_\varepsilon} (\nabla \varphi^\varepsilon)^\top A^\varepsilon \nabla (\varepsilon \eta_{\Omega_\varepsilon} U_\varepsilon w)\, dx - \varepsilon \int_{Q_\varepsilon} \Upsilon_0(\mathbf{c}^\varepsilon) \eta_{\Omega_\varepsilon} U_\varepsilon w\, dx \\ &\quad + \int_{\partial \omega_\varepsilon} \left(\frac{\alpha}{\varepsilon} [\![\varphi^\varepsilon]\!] - g^\varepsilon \right) \varepsilon [\![U_\varepsilon w]\!]\, dS_x = 0, \end{aligned}$$

where $\eta_{\Omega_\varepsilon} = 1$ at the interface $\partial \omega_\varepsilon$. Passing here to the limit as $\varepsilon \to 0$ due to (A.7) and (A.8) in cases (ii) and (iiia) of Lemma A.4, by virtue of $\varepsilon \int_{Q_\varepsilon} \varkappa \Upsilon_0(\mathbf{c}^\varepsilon) U_\varepsilon w\, dx \to 0$ due to (3.12), this leads to the following variational equality:

$$\frac{1}{|Y|} \int_{\Omega} \left\{ \int_{\Pi \cup \omega} (\nabla \varphi^0 + \nabla_y \varphi^1)^\top A \nabla_y w\, dy + \int_{\partial \omega} (\alpha [\![\varphi^1]\!]_y - g) [\![w]\!]_y\, dS_y \right\} dx = 0. \tag{3.14}$$

We take the test function $u = w$ in the cell problems (3.2) and (3.3) multiplied by $\frac{(\nabla \varphi^0)^\top}{|Y|}$ and by $\frac{1}{|Y|}$, respectively. Integrating them over Ω, we get after summation:

$$\begin{aligned} &\frac{1}{|Y|} \int_{\Omega} \left\{ \int_{\Pi \cup \omega} [(\nabla \varphi^0)^\top + (\nabla \varphi^0)^\top \partial_y \Phi + (\nabla_y \Lambda)^\top] A \nabla_y w\, dy \right. \\ &\quad \left. + \int_{\partial \omega} (\alpha [\![(\nabla \varphi^0)^\top \Phi + \Lambda]\!]_y - g) [\![w]\!]_y\, dS_y \right\} dx = 0. \end{aligned}$$

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Then, subtracting the result from the equation (3.14), after gathering the same terms $(\nabla\varphi^0)^\top A\nabla_y w$ and $g[\![w]\!]_y$ were shortened and this gives:

$$\frac{1}{|Y|}\int_\Omega\Big\{\int_{\Pi\cup\omega}[\nabla_y(\varphi^1-\Lambda-(\nabla\varphi^0)^\top\Phi)]^\top A\nabla_y w\,dy \\ +\alpha\int_{\partial\omega}[\![\varphi^1-\Lambda-(\nabla\varphi^0)^\top\Phi]\!]_y[\![w]\!]_y\,dS_y\Big\}\,dx=0, \tag{3.15}$$

where we used the identity $(\nabla\varphi^0)^\top\partial_y\Phi=\big(\nabla_y[(\nabla\varphi^0)^\top\Phi]\big)^\top$. The linear homogeneous equation (3.15) has a solution $\psi(t,x,y):=\varphi^1-\Lambda-(\nabla\varphi^0)^\top\Phi\in L^\infty(0,T;L^2(\Omega)\times H^1_\#(\Pi\cup\omega))$. We substitute $w=\psi$ into (3.15) and due to (2.5) get the lower bound

$$\frac{1}{|Y|}\int_\Omega\Big\{\underline{a}\int_{\Pi\cup\omega}|\nabla_y\psi|^2\,dy+\alpha\int_{\partial\omega}[\![\psi]\!]_y^2\,dS_y\Big\}\,dx\leqslant 0.$$

Therefore, $\psi(t,x)$ is independent on y, which implies the representation of the gradient and of the jump of φ^1 with respect to y as

$$(\nabla_y\varphi^1)^\top=(\nabla_y\Lambda)^\top+(\nabla\varphi^0)^\top\partial_y\Phi,\quad [\![\varphi^1]\!]_y=[\![\Lambda]\!]_y+(\nabla\varphi^0)^\top[\![\Phi]\!]_y. \tag{3.16}$$

Now, we substitute the expressions (3.16) into the limit equation (3.13) and obtain

$$\frac{1}{|Y|}\int_\Omega\int_{\Pi\cup\omega}\Big\{\big[(\nabla\varphi^0)^\top(I+\partial_y\Phi)+(\nabla_y\Lambda)^\top\big]A\nabla v-\varkappa\Upsilon_0(\mathbf{c}^0)v\Big\}\,dy\,dx=0. \tag{3.17}$$

Moving the terms independent on y outside the integral over $\Pi\cup\omega$ in (3.17) and introducing the notation of the averaged matrix $A^0\in\mathbb{R}^{d\times d}$ and vector $G^0\in\mathbb{R}^d$ by

$$A^0:=\frac{1}{|Y|}\int_{\Pi\cup\omega}(I+\partial_y\Phi)A\,dy,\quad (G^0)^\top:=\frac{1}{|Y|}\int_{\Pi\cup\omega}(\nabla_y\Lambda)^\top A\,dy, \tag{3.18}$$

we rewrite (3.17) in the form

$$\int_\Omega\big\{\big[(\nabla\varphi^0)^\top A^0+(G^0)^\top\big]\nabla v-\varkappa\Upsilon_0(\mathbf{c}^0)v\big\}\,dx=0\quad\text{for all } v\in H^1_0(\Omega), \tag{3.19}$$

which implies a homogeneous problem for the averaged solution $\varphi^0\in L^\infty(0,T;H^1(\Omega))$ supported by the Dirichlet boundary condition (3.7c). We cite [1, Section 3] for the homogenisation procedure of non-linear operators using a two-scale convergence.

Second, we proceed with the equation (2.10a). For functions $v_i(t,x)\in H^1(0,T;L^2(\Omega))\cap L^2(0,T;H^1_0(\Omega))$ in the domain such that $[\![v_i]\!]=0$, $i=1,\dots,n$, we test the equations (2.10a) with $\bar{c}_i=v_i$ using the expansion (3.9) and the asymptotic decoupling assumption (2.8), then pass to the limit as $\varepsilon\to 0$ analogously to (3.13) to get

$$\frac{1}{|Y|}\int_0^T\!\!\int_{\Pi\cup\omega}\left\{\left\langle\frac{\partial c_i^0}{\partial t},v_i\right\rangle_\Omega+\int_\Omega(\nabla c_i^0+\nabla_y c_i^1)^\top D\nabla v_i\,dx\right\}dy\,dt=0, \tag{3.20}$$

where we understand the time derivative in the weak sense similarly to (2.11).

To identify $\mathbf{c}^1$, we proceed similar as before. For functions in the cell $w_i(t,y)\in H^1(0,T;L^2(\Pi\cup\omega))\cap L^2(0,T;H^1_\#(\Pi\cup\omega))$, $i=1,\dots,n$, we test (2.10a) with $\bar{c}_i=\varepsilon\eta_{\Omega_\varepsilon}U_\varepsilon w_i$.

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Due to the convergences (3.7a), (3.7b), and the fact that the time derivative, non-linear and the boundary terms vanish, similarly to (3.14) gives us the limit equation as $\varepsilon \to 0$:

$$\frac{1}{|Y|}\int_0^T\!\!\int_\Omega\int_{\Pi\cup\omega}(\nabla c_i^0+\nabla_y c_i^1)^\top D\nabla_y w_i\,dy\,dx\,dt=0. \tag{3.21}$$

We multiply the cell problem (3.1) with $\frac{(\nabla c_i)^\top}{|Y|}$ and take the test function $u=w_i$:

$$\int_{\Pi\cup\omega}\left(\nabla c_i^0+\nabla_y[(\nabla c_i^0)^\top N]\right)^\top D\nabla_y w_i\,dy=0,$$

where $(\nabla c_i^0)^\top\partial_y N=(\nabla_y[(\nabla c_i^0)^\top N])^\top$ was used. Integrating it over $(0,T)$ and Ω and then subtracting from the equation (3.21), after gathering the same terms and shortening $(\nabla c_i^0)^\top D\nabla_y w_i$, we get

$$\frac{1}{|Y|}\int_0^T\!\!\int_\Omega\int_{\Pi\cup\omega}\left[\nabla_y\left(c_i^1-(\nabla c_i^0)^\top N\right)\right]^\top D\nabla_y w_i\,dy\,dx\,dt=0. \tag{3.22}$$

From the homogeneous equation (3.22), it follows that

$$(\nabla_y c_i^1)^\top=(\nabla c_i^0)^\top\partial_y N. \tag{3.23}$$

The matrix $D^0\in\mathbb{R}^{d\times d}$ of the averaged diffusivity is defined by:

$$D^0:=\frac{1}{|Y|}\int_{\Pi\cup\omega}(I+\partial_y N)D\,dy=\frac{1}{|Y|}\int_\Pi(I+\partial_y N)D\,dy, \tag{3.24}$$

because $N=-y$ and $I+\partial_y N=0$ in $\overline{\omega}\subset Y$. Therefore, we substitute (3.23) and (3.24) into (3.20) and derive the following problem describing the averaged species concentrations $\mathbf{c}^0\in[L^\infty(0,T;L^2(\Omega))\cap L^2(0,T;H^1(\Omega))]^n$ as follows:

$$\int_0^T\left\{\left\langle\frac{\partial c_i^0}{\partial t},v_i\right\rangle_\Omega+\int_\Omega(\nabla c_i^0)^\top D^0\nabla v_i\,dx\right\}dt=0. \tag{3.25}$$

subject to the Dirichlet boundary conditions (3.7c). In order to derive the initial condition $c_i^0|_{t=0}=c_i^{\mathrm{in}}$, we recall the weak form of the time derivative (2.11) with $c_i^\varepsilon|_{t=0}=c_i^{\mathrm{in}}$ and pass it to the limit as $\varepsilon\to 0$ for $\bar{c}_i|_{t=T}=0$.

The ellipticity of A^0 and D^0 follows from [4, Chapter 1, Section 3.4]. □

Now we derive a corollary from Theorem 3.1, which characterises the averaged solution.

Corollary 3.2 (Total mass balance and non-negativity) *The solution $\mathbf{c}^0$ to the averaged PNP problem* (3.4a) *satisfies the total mass balance $\sum_{i=1}^n c_i^0=C$ and the non-negativity conditions $c_i^0\geqslant 0$, $i=1,\ldots,n$.*

Proof We sum up the equations (3.4a) over $i=1,\ldots,n$ with the test functions $v_i=\sigma^0:=\sum_{i=1}^n c_i^0-C$, since $\sigma^0=\sum_{i=1}^n c_i^{\mathrm{D}}-C=0$ on $\partial\Omega$ holds, and obtain

$$\int_0^T\left\{\left\langle\frac{\partial\sigma^0}{\partial t},\sigma^0\right\rangle_\Omega+\int_\Omega(\nabla\sigma^0)^\top D^0\nabla\sigma^0\,dx\right\}dt=0. \tag{3.26}$$

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We integrate by parts with respect to time the first term in (3.26) and take into account the initial condition $\sigma^0 = 0$ at $t = 0$ since $\sum_{i=1}^n c_i^{\text{in}} = C$ is assumed, such that $\int_0^T \langle \frac{\partial \sigma^0}{\partial t}, \sigma^0 \rangle_\Omega \, dt = \frac{1}{2} \int_\Omega \sigma^0(T)^2 \, dx$. Taking into account the ellipticity condition for the averaged matrix D^0, this gives the lower estimate:

$$\frac{1}{2} \int_\Omega \sigma^0(T)^2 \, dx + \underline{d} \|\nabla \sigma^0\|^2_{L^2(0,T;L^2(\Omega))^d} \leqslant 0,$$

from which it follows $\|\sigma^0\|_c^2 := \|\sigma^0\|^2_{L^\infty(0,T;L^2(\Omega))} + \|\sigma^0\|^2_{L^2(0,T;H^1(\Omega))} = 0$, hence $\sigma^0 \equiv 0$, and the total mass balance $\sum_{i=1}^n c_i^0 = C$ holds.

Next, decomposing $c_i^0 = (c_i^0)^+ - (c_i^0)^-$ into the positive $(c_i^0)^+ = \max(0, c_i^0)$ and the negative $(c_i^0)^- = -\min(0, c_i^0)$ parts, we can insert $v_i = -(c_i^0)^-$ into (3.4a) because $(c_i^0)^- = (c_i^{\mathrm{D}})^- = 0$ on $\partial\Omega$, and derive due to the orthogonality of $(c_i^0)^+$ and $(c_i^0)^-$ that

$$\int_0^T \left\{ \left\langle \frac{\partial (c_i^0)^-}{\partial t}, (c_i^0)^- \right\rangle_\Omega + \int_\Omega (\nabla[(c_i^0)^-])^\top D^0 \nabla[(c_i^0)^-] \, dx \right\} dt = 0. \tag{3.27}$$

Henceforth, it follows

$$\frac{1}{2} \int_\Omega [(c_i^0(T))^-]^2 \, dx + \underline{d} \|\nabla[(c_i^0)^-]\|^2_{L^2(0,T;L^2(\Omega))^d} \leqslant 0, \tag{3.28}$$

thus providing that $\|(c_i^0)^-\|_c^2 = 0$ and $\mathbf{c}^0 \geqslant 0$ component wisely. This completes the proof. □

The two following corollaries suggest a next asymptotic term as $\varepsilon \to 0$.

Corollary 3.3 (Corrector due to interface fluxes) *For a weak-to-weak continuous function g_i (e.g., linear one), a corrector due to the interface fluxes is given by functions $\chi_i^\varepsilon \in L^\infty(0, T; L^2(Q_\varepsilon \cup \omega_\varepsilon)) \cap L^2(0, T; H^1(Q_\varepsilon \cup \omega_\varepsilon))$, $i = 1, \dots, n$, such that*

$$\chi_i^\varepsilon = 0 \quad \text{on } \partial\Omega, \qquad \chi_i^\varepsilon = 0 \quad \text{as } t = 0 \tag{3.29}$$

satisfying the variational equation

$$\int_0^T \left\{ \left\langle \frac{\partial \chi_i^\varepsilon}{\partial t}, \bar{c}_i \right\rangle_{Q_\varepsilon \cup \omega_\varepsilon} + \int_{Q_\varepsilon \cup \omega_\varepsilon} (\nabla \chi_i^\varepsilon)^\top D^\varepsilon \nabla \bar{c}_i \, dx \right\} dt = \int_0^T \int_{\partial\omega_\varepsilon} \varepsilon (U_\varepsilon g_i^0) [\![\bar{c}_i]\!] \, dS_x \, dt \tag{3.30}$$

for all test functions $\bar{c}_i \in H^1(0, T; L^2(Q_\varepsilon \cup \omega_\varepsilon)) \cap L^2(0, T; H^1(Q_\varepsilon \cup \omega_\varepsilon))$, where $g_i^0 := g_i([\mathbf{c}^0, \mathbf{c}^0], [\varphi^0, \varphi^0])$ and $D^\varepsilon = U_\varepsilon D$ with the matrix D from (2.8). As $\varepsilon \to 0$, the corrector obeys the convergence

$$\mathbf{c}^\varepsilon - \boldsymbol{\chi}^\varepsilon \rightharpoonup 0 \quad \text{weakly in } L^\infty(0, T; L^2(Q_\varepsilon \cup \omega_\varepsilon))^n \cap L^2(0, T; H^1(Q_\varepsilon \cup \omega_\varepsilon))^n, \tag{3.31a}$$

and the two-scale convergences

$$\left(\boldsymbol{\chi}^\varepsilon, \boldsymbol{\chi}^\varepsilon|_{\partial\omega_\varepsilon^\pm}, \frac{1}{\varepsilon} [\![\boldsymbol{\chi}^\varepsilon]\!] \right) \overset{2}{\rightharpoonup} (0, 0, 0), \qquad \nabla \boldsymbol{\chi}^\varepsilon \overset{2}{\rightharpoonup} 0 \tag{3.31b}$$

in the topology of spaces $L^2\{0, T; [L^2(\Omega) \times L^2(\Pi \cup \omega)] \cup [L^2(\Omega) \times L^2(\partial\omega)]^3\}^n$, respectively, $L^2\{0, T; [L^2(\Omega) \times L^2(\Pi \cup \omega)]^{d \times n}\}$ for the gradient.

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Proof We subtract the equation (3.30) from the inhomogeneous equation (2.10a) and apply the asymptotic decoupling (2.8) to obtain

$$\int_0^T \left\{ \left\langle \frac{\partial (c_i^\varepsilon - \chi_i^\varepsilon)}{\partial t}, \bar{c}_i \right\rangle_{Q_\varepsilon \cup \omega_\varepsilon} + \int_{Q_\varepsilon \cup \omega_\varepsilon} (\nabla (c_i^\varepsilon - \chi_i^\varepsilon))^\top D^\varepsilon \nabla \bar{c}_i \, dx \right\} dt$$
$$= \int_0^T \!\! \int_{\partial \omega_\varepsilon} \varepsilon^{1+\gamma} [g_i(\hat{\mathbf{c}}^\varepsilon, \hat{\varphi}^\varepsilon) - (U_\varepsilon g_i^0)] [\![\bar{c}_i]\!] \, dS_x \, dt + o(1), \tag{3.32}$$

where $o(1)$ expresses the lower-order asymptotic terms due to (2.8).

We pass $\varepsilon \to 0$ in the right-hand side of (3.32) based on the weak-to-weak continuity of g_i and the weak convergence $(T_\varepsilon \hat{\mathbf{c}}^\varepsilon, T_\varepsilon \hat{\varphi}^\varepsilon) \rightharpoonup ([\mathbf{c}^0, \mathbf{c}^0], [\varphi^0, \varphi^0])$ according to (3.5a) such that

$$g_i(\hat{\mathbf{c}}^\varepsilon, \hat{\varphi}^\varepsilon) \overset{2}{\rightharpoonup} g_i([\mathbf{c}^0, \mathbf{c}^0], [\varphi^0, \varphi^0]) =: g_i^0 \quad \text{in } L^2(0, T; L^2(\Omega) \times L^2(\partial \omega^\pm)). \tag{3.33}$$

It gives the zero limit of (3.32), hence (3.31a).

The two-scale convergences (3.31b) hold after applying the homogenisation result of Theorem 3.1 to the problem (3.30) for $\boldsymbol{\chi}^\varepsilon$. In doing so, we conclude with a trivial solution of the averaged problem corresponding to (3.30) because of the homogeneous boundary and initial conditions (3.29). □

Corollary 3.4 (Refined two-scale convergence) *Accounting for the corrector due to the interface fluxes in Corollary 3.3, we refine the two-scale convergence in (3.5) for $\varepsilon \to 0$ as follows:*

$$(\boldsymbol{c}^\varepsilon - \boldsymbol{\chi}^\varepsilon, (\boldsymbol{c}^\varepsilon - \boldsymbol{\chi}^\varepsilon)|_{\partial \omega_\varepsilon^\pm}) \overset{2}{\rightharpoonup} (\boldsymbol{c}^0, \boldsymbol{c}^0), \quad \nabla (\boldsymbol{c}^\varepsilon - \boldsymbol{\chi}^\varepsilon) \overset{2}{\rightharpoonup} (I + \partial_y N)^\top \nabla \boldsymbol{c}^0. \tag{3.34}$$

Indeed, the two-scale convergences (3.5) and (3.31b) together result into (3.34).

4 Discussion

The averaged PNP problem (3.4) is coupled and non-linear. However, solving first the system of linear diffusion equations (3.4a) with respect to $\mathbf{c}^0$ and substituting it into (3.4b) give the linear elliptic equation with respect to φ^0.

The scaling of non-linearities is crucial. The non-linearity $\Upsilon_j(\mathbf{c}^\varepsilon)$ in the cross-diffusion equations (2.3a) is scaled with ε^κ. The non-linear fluxes $g_i(\hat{\mathbf{c}}^\varepsilon, \hat{\varphi}^\varepsilon)$ at the phase interface on the right-hand side in the formula (2.10a) are multiplied by $\varepsilon^{1+\gamma}$. The negative values $\kappa < 0$ and $\gamma < 0$ are not admissible within the uniform *a priori* estimate of the solution $(\mathbf{c}^\varepsilon, \varphi^\varepsilon)$ established in Theorem 2.1. The case $\kappa = 0$, which describes strongly non-linear equations, is not allowed within the asymptotic method used for assertion in Theorem 3.1. In this sense, the values $\kappa > 0$ and $\gamma \geqslant 0$ taken in the paper are sharp ones.

In order to express an asymptotic order of the convergence (3.5) as $\varepsilon \to 0$, it needs to derive residual error estimates. For the larger value of $\gamma = 1$, thus avoiding the non-linearity at the interface from the homogenisation procedure, the corrector estimates are derived recently in [29].

We note that the scaling with $\gamma \geqslant 0$ yields no contribution of the interface reaction term in the macroscopic model (3.4a). For a possible remedy, in [25], we investigate the bi-domain setting of a non-linear transmission problem for the linear diffusion equation in connected domains.

However, extension of this result to the coupled system of non-linear PNP equations is not straightforward. The disconnected case is open at the moment.

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Conflict of interest

None.

References

[1] ALLAIRE, G. (1992) Homogenization and two-scale convergence. *SIAM J. Math. Anal.* **23**, 1482–1518.

[2] ALLAIRE, G., BRIZZI, R., DUFRÊCHE, J.-F., MIKELIĆ, A. & PIATNITSKI, A. (2013) Ion transport in porous media: derivation of the macroscopic equations using upscaling and properties of the effective coefficients. *Comp. Geosci.* **17**, 479–495.

[3] BELYAEV, A. G., PYATNITSKII, A. L. & CHECHKIN, G. A. (2001) Averaging in a perforated domain with an oscillating third boundary condition. *Mat. Sb.* **192**, 3–20.

[4] BENSOUSSAN, A., LIONS, J.-L. & PAPANICOLAOU, G. (1978) *Asymptotic Analysis for Periodic Structures,* North-Holland, Amsterdam, New York.

[5] BUNOIU, R. & TIMOFTE, C. (2019) Upscaling of a diffusion problem with interfacial flux jump leading to a modified Barenblatt model. *Z. Angew. Math. Mech.* **99**, e201901788.

[6] BURGER, M., SCHLAKE, B. & WOLFRAM, M.-T. (2012) Nonlinear Poisson–Nernst–Planck equations for ion flux through confined geometries. *Nonlinearity* **25**, 961–990.

[7] CIORANESCU, D., DAMLAMIAN, A., DONATO, P., GRISO, G. & ZAKI, R. (2012) The periodic unfolding method in domains with holes. *SIAM J. Math. Anal.* **44**, 718–760.

[8] CIORANESCU, D., DAMLAMIAN, A. & GRISO, G. (2008) The periodic unfolding method in homogenization. *SIAM J. Math. Anal.* **40**, 1585–1620.

[9] CIORANESCU, D., DONATO, P. & ZAKI, R. (2006) The periodic unfolding method in perforated domains. *Portugaliae Mathematica* **63**, 467–496.

[10] DESVILLETTES, L. & LORENZANI, S. (2018) Homogenization of the discrete diffusive coagulation-fragmentation equations in perforated domains. *J. Math. Anal. Appl.* **467**, 1100–1128.

[11] DONATO, P. & LE NGUYEN, K. H. (2015) Homogenization of diffusion problems with a nonlinear interfacial resistance. *Nonlinear Differ. Equ. Appl.* **22**, 1345–1380.

[12] DONATO, P., LE NGUYEN, K. H. & TARDIEU, R. (2011) The periodic unfolding method for a class of imperfect transmission problems. *J. Math. Sci.* **176**, 891–927.

[13] DONATO, P. & MONSURRÒ, S. (2004) Homogenization of two heat conductors with an interfacial contact resistance. *Anal. Appl.* **2**, 247–273.

[14] DREYER, W., GUHLKE, C. & MÜLLER, R. (2015) Modeling of electrochemical double layers in thermodynamic non-equilibrium. *Phys. Chem. Chem. Phys.* **17**, 27176–27194.

[15] EVENDIEV, M. & ZELIK, S. V. (2002) Attractors of the reaction-diffusion systems with rapidly oscillating coefficients and their homogenization. *Ann. Instit. H. Poincare* **19**, 961–989.

[16] FELLNER, K. & KOVTUNENKO, V. A. (2016) A discontinuous Poisson–Boltzmann equation with interfacial transfer: homogenisation and residual error estimate. *Appl. Anal.* **95**, 2661–2682.

[17] FRANCŮ, J. (2010) Modification of unfolding approach to two-scale convergence. *Mathematica Bohemica* **135**, 403–412.

[18] FUHRMANN, J. (2015) Comparison and numerical treatment of generalized Nernst–Planck models. *Comput. Phys. Commun.* **196**, 166–178.
[19] GAGNEUX, G. & MILLET, O. (2014) Homogenization of the Nernst–Planck–Poisson system by two-scale convergence. *J. Elast.* **114**, 69–84.
[20] GAHN, M., NEUSS-RADU, M. & KNABNER, P. (2016) Homogenization of reaction-diffusion processes in a two-component porous medium with nonlinear flux conditions at the interface. *SIAM J. App. Math.* **76**, 1819–1843.
[21] GONZÁLEZ GRANADA, J. R. & KOVTUNENKO, V. A. (2018) Entropy method for generalized Poisson–Nernst–Planck equations. *Anal. Math. Phys.* **8**, 603–619.
[22] HERZ, M., RAY, N. & KNABNER, P. (2012) Existence and uniqueness of a global weak solution of a Darcy–Nernst–Planck–Poisson system. *GAMM–Mitt.* **35**, 191–208.
[23] KHLUDNEV, A. M. & KOVTUNENKO, V. A. (2000) *Analysis of Cracks in Solids.* WIT Press, Southampton, Boston.
[24] KHOA, V. A. & MUNTEAN, A. (2019) Corrector homogenization estimates for a non-stationary Stokes–Nernst–Planck–Poisson system in perforated domains. *Commun. Math. Sci.* **17**, 705–738.
[25] KOVTUNENKO, V. A., REICHELT, S. & ZUBKOVA, A. V. (2020) Corrector estimates in homogenization of a nonlinear transmission problem for diffusion equations in connected domains. *Math. Meth. Appl. Sci.* **43**, 1838–1856.
[26] KOVTUNENKO, V. A. & ZUBKOVA, A. V. (2017) Solvability and Lyapunov stability of a two-component system of generalized Poisson–Nernst–Planck equations. In: V. Maz'ya, D. Natroshvili, E. Shargorodsky and W. L. Wendland (editors), *Recent Trends in Operator Theory and Partial Differential Equations (The Roland Duduchava Anniversary Volume). Operator Theory: Advances and Applications*, Vol. 258, Birkhaeuser, Basel, pp. 173–191.
[27] KOVTUNENKO, V. A. & ZUBKOVA, A. V. (2017) On generalized Poisson–Nernst–Planck equations with inhomogeneous boundary conditions: a-priori estimates and stability. *Math. Meth. Appl. Sci.* **40**, 2284–2299.
[28] KOVTUNENKO, V. A. & ZUBKOVA, A. V. (2018) Mathematical modeling of a discontinuous solution of the generalized Poisson–Nernst–Planck problem in a two-phase medium. *Kinet. Relat. Mod.* **11**, 119–135.
[29] KOVTUNENKO, V. A. & ZUBKOVA, A. V. (2020) Homogenization of the generalized Poisson–Nernst–Planck problem in a two-phase medium: correctors and residual error estimates. *Appl. Anal.* doi:10.1080/00036811.2019.1600676.
[30] LADYZHENSKAYA, O. A. (1985) *The Boundary Value Problems of Mathematical Physics*, Vol. 49, Springer Verlag.
[31] MEIRMANOV, A. & ZIMIN, R. (2011) Compactness result for periodic structures and its application to the homogenization of a diffusion-convection equation. *Electr. J. Differ. Equ.* **115**, 1–11.
[32] MIELKE, A., REICHELT, S. & THOMAS, M. (2014) Two-scale homogenization of nonlinear reaction-diffusion systems with slow diffusion. *J. Netw. Heterog. Media* **9**, 353–382.
[33] NGUETSENG, G. (1989) A general convergence result for a functional related to the theory of homogenization. *SIAM J. Math. Anal.* **20**, 608–623.
[34] RAY, N., ECK, CH., MUNTEAN, A. & KNABNER, P. (2011) Variable choices of scaling in the homogenization of a Nernst–Planck–Poisson problem. *Erlangen-Nürnberg: Inst. für Angewandte Mathematik* **344**.
[35] REICHELT, S. (2017) Corrector estimates for a class of imperfect transmission problems. *Asymptotic Anal.* **105**, 3–26.
[36] ROUBÍČEK, T. (2007) Incompressible ionized non-Newtonean fluid mixtures. *SIAM J. Math. Anal.* **39**, 863–890.
[37] SÁNCHEZ-PALENCIA, E. (1980) *Non-Homogeneous Media and Vibration Theory*, Springer-Verlag.
[38] SAZHENKOV, S. A., SAZHENKOVA, E. V. & ZUBKOVA, A. V. (2014) Small perturbations of two-phase fluid in pores: Effective macroscopic monophasic viscoelastic behavior. *Sib. Èlektron. Mat. Izv.* **11**, 26–51.

[39] SCHMUCK, M. & BAZANT, M. Z. (2015) Homogenization of the Poisson–Nernst–Planck equations for ion transport in charged porous media. *SIAM J. Appl. Math.* **75**, 1369–1401.
[40] TYCHONOFF, A. (1935) Ein Fixpunktsatz. *Math. Ann.* **111**, 767–776.
[41] VISINTIN, A. (2006) Towards a two-scale calculus. *ESAIM: COCV* **12**, 371–397.
[42] ZHIKOV, V. V., KOZLOV, S. M. & OLEINIK, O. A. (1994) *Homogenization of Differential Operators and Integral Functionals.* Springer-Verlag, Berlin.

Appendix A Homogenisation tools

Based on a scale transformation, we adopt the classic two-scale convergence to the two-phase domain and the interface. The corresponding criterion for a weak two-scale convergence and the compactness in two-scale topology are provided.

A.1 Scale transformation

For the asymptotic analysis, we recall here a transformation tool between the two-phase geometries $\Pi \cup \omega$ and $Q_\varepsilon \cup \omega_\varepsilon$, as well as between the interfaces $\partial\omega$ and $\partial\omega_\varepsilon$ following definitions [7, 8, 9] for Ω_ε, and [17] for the boundary layer $\Omega \setminus \Omega_\varepsilon$.

Definition A.1 The operator, describing unfolding, $f(x) \mapsto T_\varepsilon : H^1(Q_\varepsilon \cup \omega_\varepsilon) \mapsto L^2(\Omega) \times H^1(\Pi \cup \omega)$, $L^2(\partial\omega_\varepsilon) \mapsto L^2(\Omega) \times L^2(\partial\omega)$ is defined by

$$(T_\varepsilon f)(x,y) = \begin{cases} f\left(\varepsilon\lfloor \frac{x}{\varepsilon}\rfloor + \varepsilon y\right), & \text{a.e. for } x \in \Omega_\varepsilon, \\ f(x), & \text{a.e. for } x \in \Omega \setminus \Omega_\varepsilon \end{cases} \quad \text{and } y \in Y, \tag{A.1}$$

and the operator, describing averaging, $u(x,y) \mapsto U_\varepsilon : L^2(\Omega) \times H^1(\Pi \cup \omega) \mapsto H^1[(\bigcup_{l\in I^\varepsilon} \Pi_\varepsilon^l) \cup \omega_\varepsilon \cup (\Omega \setminus \Omega_\varepsilon)]$, $L^2(\Omega) \times L^2(\partial\omega) \mapsto L^2(\partial\omega_\varepsilon)$ is set by:

$$(U_\varepsilon u)(x) = \begin{cases} \dfrac{1}{|Y|} \displaystyle\int_{\Pi\cup\omega} u\left(\varepsilon\lfloor \tfrac{x}{\varepsilon}\rfloor + \varepsilon z, \left\{\tfrac{x}{\varepsilon}\right\}\right) dz, & \text{a.e. for } x \in \Omega_\varepsilon, \\ \dfrac{1}{|Y|} \displaystyle\int_{\Pi\cup\omega} u(x,y)\, dy, & \text{a.e. for } x \in \Omega \setminus \Omega_\varepsilon, \end{cases} \tag{A.2}$$

where $|Y|$ stands for the Hausdorff measure of the set Y in $\mathbb{R}^d$, and $|Y| = 1$ in the case of $Y = (0,1)^d$.

The operators T_ε and U_ε are defined well for admissible functions on the interface, since (A.1) is fulfilled on the subset $x \in \partial\omega_\varepsilon \subset \Omega_\varepsilon$, and (A.2) holds for all $y \in \Pi \cup \omega \cup \partial\omega = Y$. By this, U_ε is a left inverse operator of T_ε according to Lemma A.2 (i), which is also right inverse in the special cases accounting in Lemma A.2 (ii). We note that, generally, $U_\varepsilon u$ is discontinuous across the interface $\partial\omega_\varepsilon$, the cell boundaries ∂Y_ε^l and $\partial\Omega_\varepsilon$.

The properties of the operators given in (A.1) and (A.2) are collected below in Lemma A.2 for the reader convenience, see [7, 8, 9] and extensions to multi-phase domains in [29].

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Lemma A.2 (Properties of the operators T_ε and U_ε) *For functions $f(x) \in H^1(Q_\varepsilon \cup \omega_\varepsilon)$ and $h(x) \in L^2(\partial\omega_\varepsilon)$, the following properties hold:*

(i) *invertibility of T_ε: $(U_\varepsilon T_\varepsilon)f(x) = f(x)$ for $x \in Q_\varepsilon \cup \omega_\varepsilon$ and $(U_\varepsilon T_\varepsilon)h(x) = h(x)$ for $x \in \partial\omega_\varepsilon$;* (A.3a)

(ii) *invertibility of U_ε: if $u(y)$ is constant for $x \in Q_\varepsilon \cup \omega_\varepsilon$ or periodic function of the argument $y \in \Pi \cup \omega$ for $x \in \Pi_\varepsilon \cup \omega_\varepsilon$, then:*

$$(T_\varepsilon U_\varepsilon)u(x, y) = u(y); \tag{A.3b}$$

(iii) *composition rule: $T_\varepsilon(\mathcal{F}(f)) = \mathcal{F}(T_\varepsilon f)$ and $T_\varepsilon(\mathcal{F}(h)) = \mathcal{F}(T_\varepsilon h)$ for any elementary function $\mathcal{F}$ composed of simple functions;* (A.3c)

(iv) *chain rule: $\varepsilon T_\varepsilon(\nabla f)(x, y) = \nabla_y(T_\varepsilon f)(x, y)$ for $(x, y) \in \Omega \times (\Pi \cup \omega)$;* (A.3d)

(v) *integration rules:*

$$\int_{Q_\varepsilon \cup \omega_\varepsilon} f(x)\, dx = \frac{1}{|Y|} \int_\Omega \int_{\Pi \cup \omega} (T_\varepsilon f)(x, y)\, dy\, dx, \tag{A.3e}$$

$$\int_{\partial\omega_\varepsilon} h(x)\, dS_x = \frac{1}{\varepsilon|Y|} \int_\Omega \int_{\partial\omega} (T_\varepsilon h)(x, y)\, dS_y\, dx; \tag{A.3f}$$

(vi) *boundedness of T_ε:*

$$\int_{Q_\varepsilon \cup \omega_\varepsilon} f^2(x)\, dx = \frac{1}{|Y|} \int_\Omega \int_{\Pi \cup \omega} (T_\varepsilon f)^2(x, y)\, dy\, dx, \tag{A.3g}$$

$$\int_{Q_\varepsilon \cup \omega_\varepsilon} |\nabla f|^2(x)\, dx = \frac{1}{\varepsilon^2|Y|} \int_\Omega \int_{\Pi \cup \omega} |\nabla_y(T_\varepsilon f)|^2(x, y)\, dy\, dx, \tag{A.3h}$$

$$\int_{\partial\omega_\varepsilon} h^2(x)\, dS_x = \frac{1}{\varepsilon|Y|} \int_\Omega \int_{\partial\omega} (T_\varepsilon h)^2(x, y)\, dS_y\, dx. \tag{A.3i}$$

The properties of operators T_ε and U_ε are useful in the following to deal with convergences in micro- and macro-scales.

A.2 Two-scale convergence

We start with the classic definition of a two-scale convergence from [1, Definition 1.1]: a parametric family $(f^\varepsilon)_{\varepsilon\in\mathbb{R}_+}(x) \in L^2(Q_\varepsilon \cup \omega_\varepsilon)$ two-scale converges weakly to $f^0(x, y) \in L^2(\Omega) \times L^2(\Pi \cup \omega)$ as $\varepsilon \to 0$ if

$$\int_{Q_\varepsilon \cup \omega_\varepsilon} f^\varepsilon(x)\psi(x, \{\frac{x}{\varepsilon}\})\, dx \to \frac{1}{|Y|} \int_\Omega \int_{\Pi \cup \omega} f^0(x, y)\psi(x, y)\, dy\, dx \tag{A.4}$$

for any smooth function $\psi : \Omega \times Y \mapsto \mathbb{R}$ that is periodic through ∂Y with respect to the second argument, that is, $\psi|_{y_k=0} = \psi|_{y_k=1}$, $k = 1, \ldots, d$. Following the approach of [32, 41], further we adopt the two-scale convergence to the two-phase domains and their interfaces.

Lemma A.3 (Convergence criterion) *(i) Let $(f^\varepsilon)_{\varepsilon\in\mathbb{R}_+}(x) \in L^2(Q_\varepsilon \cup \omega_\varepsilon)$. Its weak two-scale convergence to $f^0(x, y)$ as the parameter $\varepsilon \to 0$:*

$$f^\varepsilon \overset{2}{\rightharpoonup} f^0 \quad \text{in } L^2(\Omega) \times L^2(\Pi \cup \omega)$$

is determined by $T_\varepsilon f^\varepsilon \rightharpoonup f^0$ weakly in $L^2(\Omega) \times L^2(\Pi \cup \omega)$.

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(ii) *Let* $(f^\varepsilon)_{\varepsilon\in\mathbb{R}_+}(x) \in L^2(\partial\omega_\varepsilon)$ *be a parametric family given on the interface. A weak two-scale convergence* $f^\varepsilon \overset{2}{\rightharpoonup} f^0$ *in* $L^2(\Omega)\times L^2(\partial\omega)$ *is determined by* $T_\varepsilon f^\varepsilon \rightharpoonup f^0$ *weakly in* $L^2(\Omega)\times L^2(\partial\omega)$ *as* $\varepsilon \to 0$.

(iii) *The strong two-scale convergence* $f^\varepsilon \overset{2}{\to} f^0$ *is determined by* $T_\varepsilon f^\varepsilon \to f^0$ *in the strong topology of the respective function space.*

Proof Combining together the test functions $u \in L^2(\Pi\cup\omega)$ and $q \in L^2(\Omega)$ from Lemma A.4 (ia) and (ib) below as $\psi(x,y) = q(x)u(y)$ and $\psi(x,\{\frac{x}{\varepsilon}\}) = q(x)(U_\varepsilon u)(x)$, from (A.5) and (A.6) it follows (A.4). In particular, for u periodic on ∂Y, this formula coincides with the classic definition. □

Applying the integration rules (A.3e), (A.3f), and (A.3h) from Lemma A.2, we derive:

Lemma A.4 (Weak two-scale convergences) *(i) For* $(f^\varepsilon)_{\varepsilon\in\mathbb{R}_+} \in L^2(Q_\varepsilon\cup\omega_\varepsilon)$ *in the two-phase domain, if* $f^\varepsilon(x) \overset{2}{\rightharpoonup} f^0(x,y)$ *in* $L^2(\Omega)\times L^2(\Pi\cup\omega)$, *then*

(ia)

$$\int_{Q_\varepsilon\cup\omega_\varepsilon} f^\varepsilon(U_\varepsilon u)\,dx \longrightarrow \frac{1}{|Y|}\int_\Omega\int_{\Pi\cup\omega} f^0 u\,dy\,dx, \tag{A.5}$$

for all test functions $u(y) \in L^2(\Pi\cup\omega)$ *in the cell;*

(ib)

$$\int_{Q_\varepsilon\cup\omega_\varepsilon} f^\varepsilon q\,dx \longrightarrow \frac{1}{|Y|}\int_\Omega\int_{\Pi\cup\omega} f^0 q\,dy\,dx \tag{A.6}$$

for all test functions $q(x) \in L^2(\Omega)$ *in the domain.*

(ii) *For* $(f^\varepsilon)_{\varepsilon\in\mathbb{R}_+} \in L^2(\partial\omega_\varepsilon)$ *at interface, if* $f^\varepsilon(x) \overset{2}{\rightharpoonup} f^0(x,y)$ *in* $L^2(\Omega)\times L^2(\partial\omega^\pm)$, *then*

$$\int_{\partial\omega_\varepsilon^\pm} f^\varepsilon(\varepsilon U_\varepsilon u)\,dS_x \longrightarrow \frac{1}{|Y|}\int_\Omega\int_{\partial\omega^\pm} f^0 u\,dS_y\,dx, \tag{A.7}$$

for all test functions $u(y) \in L^2(\partial\omega^\pm)$ *at the interface.*

(iii) *Let* $T_\varepsilon A^\varepsilon = A$ *for a d-by-d matrix A, where the notation* $A^\varepsilon := U_\varepsilon A$. *If the gradient* $\nabla f^\varepsilon(x) \overset{2}{\rightharpoonup} \tilde{f}(x,y)$ *in* $[L^2(\Omega)\times L^2(\Pi\cup\omega)]^d$, *then*

(iiia)

$$\int_{Q_\varepsilon\cup\omega_\varepsilon} (\nabla f^\varepsilon)^\top A^\varepsilon \nabla(\varepsilon\eta_{\Omega_\varepsilon} U_\varepsilon u)\,dx \longrightarrow \frac{1}{|Y|}\int_\Omega\int_{\Pi\cup\omega} \tilde{f}^\top A\nabla_y u\,dy\,dx, \tag{A.8}$$

for all test functions $u(y) \in H^1_\#(\Pi\cup\omega)$ *in the cell, where* $\eta_{\Omega_\varepsilon}$ *is a cut-off function supported in* Ω_ε, *equals one outside an* ε*-neighborhood of* $\partial\Omega_\varepsilon$, *and* $\varepsilon|\nabla\eta_{\Omega_\varepsilon}| \leqslant \mathrm{const}$.

(iiib)

$$\int_{Q_\varepsilon\cup\omega_\varepsilon} (\nabla f^\varepsilon)^\top A^\varepsilon \nabla q\,dx \longrightarrow \frac{1}{|Y|}\int_\Omega\int_{\Pi\cup\omega} \tilde{f}^\top A\nabla q\,dy\,dx, \tag{A.9}$$

for all test functions $q(x) \in H^1(\Omega)$ *in the domain.*

Proof In fact, the results (i) and (ii) are already known in the cited literature [1]. For the assertion (iii), case (iiia), by periodicity of the test function, we ensure the continuity of $U_\varepsilon u$ across the local

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cell boundaries ∂Y_ε^l, $l \in I^\varepsilon$, hence $\eta_{\Omega_\varepsilon} U_\varepsilon u \in H^1(Q_\varepsilon \cup \omega_\varepsilon)$ for the cut-off function $\eta_{\Omega_\varepsilon}$ supported in Ω_ε. Therefore, from the integration rule (A.3h), it follows (A.8) due to the chain rule $\nabla(\varepsilon U_\varepsilon u) = U_\varepsilon(\nabla_y u)$ and the assumption $T_\varepsilon A^\varepsilon = A$, where $(\eta_{\Omega_\varepsilon} - 1)$ and $\varepsilon \nabla \eta_{\Omega_\varepsilon}$ are bounded and have non-zero support of the asymptotic order $O(\varepsilon)$. The case (iiib) is based on (A.6). □

The following Lemma A.5 is a generalisation of [1, Proposition 1.14] for the two-phase domain. For a related strong compactness result, see in [31].

Lemma A.5 (Compactness in the two-scale topology) *(i) Let $(f^\varepsilon)_{\varepsilon\in\mathbb{R}_+}(x) \in L^2(Q_\varepsilon \cup \omega_\varepsilon)$. If the uniform L^2-estimate holds*

$$\|f^\varepsilon\|^2_{L^2(Q_\varepsilon\cup\omega_\varepsilon)} \leqslant K, \quad K > 0, \tag{A.10}$$

then there exists $f^0(x, y) \in L^2(\Omega) \times L^2(\Pi \cup \omega)$ and a sequence of parameters ε, such that $f^\varepsilon(x) \overset{2}{\rightharpoonup} f^0(x, y)$ in $L^2(\Omega) \times L^2(\Pi \cup \omega)$ as $\varepsilon \to 0$ according to Lemma A.3.

(ii) Let $(f^\varepsilon)_{\varepsilon\in\mathbb{R}_+}(x) \in H^1(Q_\varepsilon \cup \omega_\varepsilon)$. If the H^1-estimate holds

$$\|f^\varepsilon\|^2_{L^2(Q_\varepsilon\cup\omega_\varepsilon)} + \varepsilon^2\|\nabla f^\varepsilon\|^2_{L^2(Q_\varepsilon\cup\omega_\varepsilon)^d} \leqslant K, \quad K > 0, \tag{A.11}$$

then there exists $f^0(x, y) \in L^2(\Omega) \times H^1(\Pi \cup \omega)$ and a sequence of parameters ε such that $T_\varepsilon f^\varepsilon \rightharpoonup f^0$ weakly in $L^2(\Omega) \times H^1(\Pi \cup \omega)$, hence as $\varepsilon \to 0$

$$\big(f^\varepsilon, \varepsilon\nabla f^\varepsilon, f^\varepsilon|_{\partial\omega_\varepsilon^\pm}, [\![f^\varepsilon]\!]\big)(x) \overset{2}{\rightharpoonup} \big(f^0, \nabla_y f^0, f^0|_{\partial\omega^\pm}, [\![f^0]\!]_y\big)(x, y) \tag{A.12}$$

in $[L^2(\Omega) \times L^2(\Pi \cup \omega)]^{1+d} \times [L^2(\Omega) \times L^2(\partial\omega)]^3$.

(iii) For $(f^\varepsilon)_{\varepsilon\in\mathbb{R}_+}(x) \in H^1(Q_\varepsilon \cup \omega_\varepsilon)$, if the stronger than (A.11) estimate holds

$$\|f^\varepsilon\|^2_{L^2(Q_\varepsilon\cup\omega_\varepsilon)} + \|\nabla f^\varepsilon\|^2_{L^2(Q_\varepsilon\cup\omega_\varepsilon)^d} + \frac{\beta}{\varepsilon}\|[\![f^\varepsilon]\!]\|^2_{L^2(\partial\omega_\varepsilon)} \leqslant K, \quad K > 0, \tag{A.13}$$

with fixed binary $\beta \in \{0, 1\}$, then there exist $f^0(x) \in H^1(\Omega)$ and $f^1(x, y) \in L^2(\Omega) \times H^1_\#(\Pi \cup \omega)$ such that as $\varepsilon \to 0$ (A.12) reads

$$\big(f^\varepsilon, \varepsilon\nabla f^\varepsilon, f^\varepsilon|_{\partial\omega_\varepsilon^\pm}, [\![f^\varepsilon]\!]\big)(x) \overset{2}{\rightharpoonup} \big(f^0, 0, f^0, 0\big)(x),$$

and additionally it holds

$$\Big(\nabla f^\varepsilon, \frac{\beta}{\varepsilon}[\![f^\varepsilon]\!]\Big)(x) \overset{2}{\rightharpoonup} \big(\nabla f^0(x) + \nabla_y f^1(x, y), \beta[\![f^1(x, y)]\!]_y\big) \tag{A.14}$$

in $[L^2(\Omega) \times L^2(\Pi \cup \omega)]^d \times [L^2(\Omega) \times L^2(\partial\omega)]$.

(iiia) If $f^\varepsilon = f^{\mathrm{D}}$ on $\partial\Omega$ for all ε, then $f^0 = f^{\mathrm{D}}$ on $\partial\Omega$.

Proof Let functions $f^\varepsilon(x)$ given with respect to the macro-variable x be bounded uniformly in ε in the norm corresponding to either (A.10) or (A.11). Their images $T_\varepsilon f^\varepsilon(x, y)$ are also uniformly bounded with respect to the two-scale variable (x, y) according to the integration rules (A.3g), (A.3h) and (A.3i). Then the assertions (i) and (ii) follow in a usual way by sequential compactness and applying the standard trace theorem.

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(iii) Let $\beta = 1$. For $\varepsilon \leqslant 1$, the estimate (A.13) implies also (A.11). Therefore, the assertion (ii) provides existence of $f^0(x, y)$ such that

$$T_\varepsilon f^\varepsilon \rightharpoonup f^0 \quad \text{in } L^2(\Omega) \times H^1(\Pi \cup \omega) \text{ as } \varepsilon \to 0. \tag{A.15}$$

From the other side, applying the integration rules (A.3h), (A.3f) and (A.3i) from (A.13), it follows the estimate with respect to the two-scale variable:

$$\|T_\varepsilon f^\varepsilon\|^2_{L^2(\Omega)\times L^2(\Pi\cup\omega)} + \frac{1}{\varepsilon^2}\|\nabla_y(T_\varepsilon f^\varepsilon)\|^2_{[L^2(\Omega)\times L^2(\Pi\cup\omega)]^d} + \frac{1}{\varepsilon^2}\|[\![T_\varepsilon f^\varepsilon]\!]_y\|^2_{L^2(\Omega)\times L^2(\partial\omega)} \leqslant K.$$

By the compactness principle, there exist $\tilde{f}(x, y) \in (L^2(\Omega) \times L^2(\Pi \cup \omega))^d$ and $f^2(x, y) \in L^2(\Omega) \times L^2(\partial\omega)$, and a sequence of f^ε such that

$$T_\varepsilon(\nabla f^\varepsilon) = \nabla_y\big(\frac{1}{\varepsilon} T_\varepsilon f^\varepsilon\big) \rightharpoonup \tilde{f}, \quad \frac{1}{\varepsilon}[\![T_\varepsilon f^\varepsilon]\!]_y \rightharpoonup f^2 \quad \text{as } \varepsilon \to 0, \tag{A.16}$$

where we have used the chain rule (A.3d). In the sense of the two-scale convergence, (A.15) and (A.16) imply that

$$(f^\varepsilon, \nabla f^\varepsilon, \frac{1}{\varepsilon}[\![f^\varepsilon]\!]) \overset{2}{\rightharpoonup} (f^0, \tilde{f}, f^2). \tag{A.17}$$

In the following, we specify functions $f^0, \tilde{f}$ and f^2 in (A.17), which will justify (A.14).

The definition of the weak convergence in (A.16) implies that:

$$\int_\Omega \int_{\Pi\cup\omega} \left(\nabla_y \left(\frac{1}{\varepsilon} T_\varepsilon f^\varepsilon\right) - \tilde{f}\right) v \, dy \, dx \to 0 \quad \text{as } \varepsilon \to 0, \tag{A.18}$$

for all $v \in L^2(\Omega) \times L^2(\Pi \cup \omega)$. Inserting in (A.18) the test function $v = \varepsilon w$ with an arbitrary $w \in L^2(\Omega) \times L^2(\Pi \cup \omega)$, we derive

$$\int_\Omega \int_{\Pi\cup\omega} \big(\nabla_y(T_\varepsilon f^\varepsilon) - \varepsilon\tilde{f}\big) w \, dy \, dx \to 0 \quad \text{as } \varepsilon \to 0.$$

Since $\varepsilon\tilde{f} \to 0$, the substitution of $w = \nabla_y(T_\varepsilon f^\varepsilon)$ follows that $\nabla_y(T_\varepsilon f^\varepsilon) \to 0$ strongly. On the other hand, (A.15) implies the weak convergence $\nabla_y(T_\varepsilon f^\varepsilon) \rightharpoonup \nabla_y f^0$, thus concluding that $\nabla_y f^0 = 0$ and $f^0(x) \in L^2(\Omega)$ does not depend on y.

Using another chain rule, $\mathrm{div}(U_\varepsilon q) = U_\varepsilon(\mathrm{div}\, q + \frac{1}{\varepsilon}\mathrm{div}_y q)$ for $x \in \Omega_\varepsilon$ and $\mathrm{div}(U_\varepsilon q) = U_\varepsilon(\mathrm{div}\, q)$ for $x \in \Omega \setminus \Omega_\varepsilon$ according to the definition (A.2), the following Green's formula holds:

$$\int_{Q_\varepsilon\cup\omega_\varepsilon} \big((\nabla f^\varepsilon)^\top (U_\varepsilon q) + f^\varepsilon U_\varepsilon(\mathrm{div}\, q)\big) \, dx = -\int_{\partial\omega_\varepsilon} [\![f^\varepsilon (U_\varepsilon q)^\top]\!] \nu \, dS_x, \tag{A.19}$$

for all vector functions $q(x, y) \in (H^1_0(\Omega) \times H^1_\#(\Pi \cup \omega))^d$ provided by $\mathrm{div}_y q(x, \cdot) = 0$ for $x \in \Omega$. Based on the integration rules (A.3e), (A.3f), and the chain rule (A.3d), the last equation is rewritten with respect to the two-scale variable as

$$\int_\Omega \int_{\Pi\cup\omega} \Big(\frac{1}{\varepsilon} \big(\nabla_y (T_\varepsilon f^\varepsilon)\big)^\top q + (T_\varepsilon f^\varepsilon) \operatorname{div} q \Big)\, dy\, dx$$
$$= - \int_\Omega \int_{\partial\omega} \frac{1}{\varepsilon} [\![T_\varepsilon f^\varepsilon]\!]_y q^\top \nu \, dS_y \, dx, \tag{A.20}$$

for the smaller set of the test functions such that $[\![q^\top]\!]_y \nu = 0$ for $y \in \partial\omega$. Passing (A.20) to the limit as $\varepsilon \to 0$ in virtue of the convergences (A.15) and (A.16), we get

$$I := \int_\Omega \int_{\Pi\cup\omega} \big((\tilde{f})^\top q + f^0 \operatorname{div} q \big)\, dy\, dx = - \int_\Omega \int_{\partial\omega} f^2 q^\top \nu \, dS_y \, dx. \tag{A.21}$$

The substitution of $\tilde{q} \in (C_0^\infty(\Omega) \times H^1_\#(\Pi\cup\omega))^d$ with $\operatorname{div}_y \tilde{q} = 0$ and $\tilde{q}^\top \nu = 0$ on $\partial\omega$ into (A.21), such that its right-hand side vanishes, provides the generalised gradient $\nabla f^0 \in C_0^\infty(\Omega)^*$ satisfying

$$\int_\Omega \int_{\Pi\cup\omega} \tilde{f}^\top \tilde{q} \, dy\, dx = - \int_\Omega \int_{\Pi\cup\omega} f^0 \operatorname{div} \tilde{q} \, dy\, dx$$
$$= \Big\langle \nabla f^0, \int_{\Pi\cup\omega} \tilde{q}\, dy \Big\rangle_{(C_0^\infty(\Omega)^*, C_0^\infty(\Omega))}. \tag{A.22}$$

We denote by $\theta(x) := \int_{\Pi\cup\omega} \tilde{q}\, dy$. The left-hand side of (A.22) builds a linear continuous form, and the right-hand side implies the duality $\langle \nabla f^0, \theta \rangle_{(C_0^\infty(\Omega)^*, C_0^\infty(\Omega))}$ for arbitrary $\theta \in L^2(\Omega)$ according to [1, Lemma 2.10].

Indeed, for the unit vectors $e^k \in \mathbb{R}^d$ with $e^k_i = \delta_{ki}$, for $i, k = 1, \ldots, d$, there exists the unique solution $V^k(y) \in H^1_\#(\Pi\cup\omega)^d$, $p^k(y) \in L^2(\Pi\cup\omega)$ to the following Stokes problem on the unit cell:

$$\operatorname{div}_y V^k = 0 \quad \text{in } \Pi\cup\omega, \qquad V^k = 0 \quad \text{on } \partial\omega^\pm,$$
$$\int_{\Pi\cup\omega} \big\{ (\partial_y V^k)^\top \partial_y u - p^k \operatorname{div}_y u \big\}\, dy = (e^k)^\top \int_{\Pi\cup\omega} u\, dy, \tag{A.23}$$

for all test functions $u \in H^1_\#(\Pi\cup\omega)^d$ with $\operatorname{div}_y u = 0$. Inserting $u = V^k$ into (A.23) yields the identity:

$$\|\partial_y V^k\|^2_{L^2(\Pi\cup\omega)^{d\times d}} = (e^k)^\top \int_{\Pi\cup\omega} V^k \, dy,$$

and $\int_{\Pi\cup\omega} \tilde{q}\, dy = \theta$ for the components $\tilde{q} = (\tilde{q}_1, \ldots, \tilde{q}_k)$ defined by

$$\tilde{q}_k(x, y) := \theta_k(x) \frac{(e^k)^\top V^k(y)}{\|\partial_y V^k\|^2_{L^2(\Pi\cup\omega)^{d\times d}}}.$$

Henceforth, $\nabla f^0 \in L^2(\Omega)^d$ with $f^0 \in H^1(\Omega)$, and

$$\int_\Omega \int_{\Pi\cup\omega} (\tilde{f} - \nabla f^0)^\top \tilde{q}\, dy\, dx = 0.$$

Consequently, by the Helmholtz theorem applied separately for test functions with $\tilde{q}(x, \cdot) = 0$ in ω, and with $\tilde{q}(x, \cdot) = 0$ in Π for $x \in \Omega$, there exists $f^1(x, y) \in L^2(\Omega) \times H^1(\Pi\cup\omega)$ such that

$$\tilde{f} - \nabla f^0 = \nabla_y f^1. \tag{A.24}$$

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Inserting $\tilde{f}$ from (A.24) into the expression of I in (A.21) and integrating it by parts lead to the following variational equation:

$$I=\int_{\Omega}\int_{\Pi\cup\omega}\big((\nabla_y f^1+\nabla f^0)^\top q+f^0\operatorname{div} q\big)\,dy\,dx=\int_{\partial\Omega}\int_{\Pi\cup\omega} f^0 q^\top \nu\,dy\,dS_x$$
$$+\int_{\Omega}\Big\{-\int_{\Pi\cup\omega} f^1\operatorname{div}_y q\,dy-\int_{\partial\omega}[\![f^1]\!]_y q^\top\nu\,dS_y+\int_{\partial Y} f^1 q^\top\nu\,dS_y\Big\}\,dx \qquad \text{(A.25)}$$

for all vector functions $q\in(H^1(\Omega)\times H^1(\Pi\cup\omega))^d$. For the test functions such that $q=0$ for $x\in\partial\Omega$, $\operatorname{div}_y q=0$ for $x\in\Omega$, and q is periodic for $y\in\partial Y$, from the last equality compared with (A.21), we obtain

$$f^2=[\![f^1]\!]_y \qquad \text{(A.26)}$$

and the periodicity of f^1 for $y\in\partial Y$. Inserting the identities (A.24) and (A.26) into (A.17) proves (A.14).

In the other case of $\beta=0$, instead of (A.19), we start with Green's formula

$$\int_{Q_\varepsilon\cup\omega_\varepsilon}\big((\nabla f^\varepsilon)^\top(U_\varepsilon q)+f^\varepsilon U_\varepsilon(\operatorname{div} q)\big)\,dx=0,$$

for all vector functions $q\in(H^1_0(\Omega)\times H^1_\#(\Pi\cup\omega))^d$ such that $\operatorname{div}_y q=0$ for $x\in\Omega$ and $q^\top\nu=0$ for $x\in\partial\omega$. Then, we repeat word by word the above argument with the test functions such that $q^\top\nu=0$ on $\partial\omega$, thus deriving (A.24) and the periodicity of f^1. Note that this consideration says nothing about the convergence of $[\![f^\varepsilon]\!]$ in (A.14), whereas if $\beta=1$, then on the macroscopic level the jump on $\partial\omega_\varepsilon$ is zero.

(iiia) If $f^\varepsilon=f^{\mathrm{D}}$ on $\partial\Omega$, then in the right-hand side of (A.19), we consider the additional summand $\int_{\partial\Omega} f^{\mathrm{D}}(U_\varepsilon q)^\top\nu\,dS_x$ for $q(x,y)\in(H^1(\Omega)\times H^1_\#(\Pi\cup\omega))^d$ with $\operatorname{div}_y q(x,\cdot)=0$. This term has the following limit $\frac{1}{|Y|}\int_\Omega\int_{\Pi\cup\omega} f^{\mathrm{D}} q^\top\nu\,dy\,dS_x$ as $\varepsilon\to 0$. Therefore, using the convergences (A.14), for test functions $q(x,y)$ with arbitrary boundary values on $\partial\Omega$ instead of (A.21), we get the limit:

$$I=\int_{\Omega}\int_{\Pi\cup\omega}\big((\nabla_y f^1+\nabla f^0)^\top q+f^0\operatorname{div} q\big)\,dy\,dx$$
$$=-\int_{\Omega}\int_{\partial\omega}[\![f^1]\!]_y q^\top\nu\,dS_y\,dx+\int_{\partial\Omega}\int_{\Pi\cup\omega} f^{\mathrm{D}} q^\top\nu\,dy\,dS_x.$$

On the other side, after integration by parts in the double integral over $\Omega\times(\Pi\cup\omega)$ similarly to (A.25), due to $\operatorname{div}_y q=0$ and the periodicity of $q(x,\cdot)$ on ∂Y, we obtain

$$I=-\int_{\Omega}\int_{\partial\omega}[\![f^1]\!]_y q^\top\nu\,dS_y\,dx+\int_{\partial\Omega}\int_{\Pi\cup\omega} f^0 q^\top\nu\,dy\,dS_x.$$

Therefore, comparing the last two equations provides the identity $f^0=f^{\mathrm{D}}$ on the boundary $\partial\Omega$. □

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