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Homogenization of the Generalized Poisson–Nernst–Planck Problem in Two-Phase Medium: the Corrector Due to Nonlinear Interface Condition

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Abstract. The paper deals with homogenization of the generalized Poisson–Nernst–Planck problem stated in the disconnected domain composed of solid and pore phases. The nonlinear cross-diffusion transport equations are coupled with the Stokes flow model. At the interface between two phases, field variables are discontinuous allowing jumps, and nonlinear interface conditions describing electro-chemical reactions are taken into consideration. The first-order asymptotic corrector corresponding to the non-periodic interface data is derived rigorously and justified by residual error estimates within the homogenization procedure.

INTRODUCTION

The generalized Poisson–Nernst–Planck (PNP) model describes cross-diffusion transport of multiple charged species coupled with the overall electrostatic distribution in a multi-phase medium and the Stokes flow model. Together with the entropy variables describing electro-chemical and pressure phenomena, governing relations obey the structure of a gradient flow [1]. From the thermodynamic point of view, accounting for the pressure as described in [2] allows the species concentrations to satisfy the total mass balance and the positivity conditions within the Gibbs simplex. For the flow modeling and analysis we refer to [3, 4, 5].

The reference two-phase medium obeys micro-structures consisting of solid and pore phases which are separated by a thin interface. In the disconnected domain, field variables allow discontinuity with jumps across the interface, see the relevent variational theory in [6]. At the interface, mixed Neumann and Robin type inhomogeneous conditions are stated, which are due to electrochemical reactions that may occur here. The diffusion fluxes and the electric current are assumed continuous across the phase interface, and most importantly, the diffusion fluxes have to be described by nonlinear functions of the field variables for consistency.

From a mathematical viewpoint, the generalized PNP problem implies the doubly nonlinear system of partial differential equations of mixed parabolic-elliptic type. Based on the Tikhonov–Schauder fixed point theorem, its solvability and uniqueness properties were established by the authors [7, 8, 9], supported by energy a-priori estimates and entropy dissipation inequality for stability of the system. For the Lyapunov analysis of dynamic stability we refer to [10], and to [11, 12] for homogenization of diffusion problems. The steady-state Poisson–Boltzmann equations over a two-phase periodic domain under homogeneous interface conditions were investigated in [13].

In the previous work [14], homogenization procedure for the generalized PNP problem stated in the periodic two-phase domain was carried out, based on discontinuous prolongation from the perforated domain inside solid particles and extending the periodic unfolding technique to the two-phase domain based on the two-scale unfolding and averaging operators. As the result of the homogenization, an averaged mono-domain model was obtained consisting of linear parabolic-elliptic equations and supported by first-order correctors and residual error estimates. These corrector

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terms were expressed by solutions of local problems in a unit cell and appeared due to the periodic electric current at the phase interface, the periodic matrix of permittivity, and the periodic matrices of diffusivity.

In the present contribution we continue this approach and extend the previous result for non-periodic data due to the inhomogenous interface conditions depending on the solution itself. We get the interface corrector and prove the corresponding residual error estimate. In contrast, in the non-periodic case the corrector term is not local and it is given by a solution of an auxiliary diffusion problem.

GENERALIZED PNP PROBLEM

We start with the description of periodic geometry. Let the unit cell $Y = (0,1)^d$ ($d \in \mathbb{N}$) consist of an isolated part $\overline{\omega} \subset Y$ (the solid particle) and the connected part $\Pi := Y \setminus \overline{\omega}$ (the pore) separated by a smooth connected manifold $\partial\omega$ (the interface) of co-dimension one with the unit normal vector ν outward ω. For a small homogenization parameter $\varepsilon \in \mathbb{R}_+$, spacial points $x \in \mathbb{R}^d$ can be decomposed as $x = \varepsilon \left\lfloor \frac{x}{\varepsilon} \right\rfloor + \varepsilon \left\{ \frac{x}{\varepsilon} \right\}$ into the floor part $\left\lfloor \frac{x}{\varepsilon} \right\rfloor \in \mathbb{Z}^d$ and the fractional part $\left\{ \frac{x}{\varepsilon} \right\} \in Y$. Then local cells Y^l_ε with indices $l \in \mathbb{N}$ are counted by a natural ordering such that $x \in Y^l_\varepsilon$ and $\left\{ \frac{x}{\varepsilon} \right\} \in Y$.

Let Ω be a domain in $\mathbb{R}^d$ with the smooth boundary $\partial\Omega$, and $\Omega_\varepsilon := \operatorname{int}(\bigcup_{l \in I^\varepsilon} \overline{Y^l_\varepsilon}) \subset \Omega$ be the union of those cells Y^l_ε that are contained in Ω with the corresponding set of indices I^ε. After scaling $y = \left\{ \frac{x}{\varepsilon} \right\}$, the local coordinate $y \in \omega$ determines the solid particle such that $\left\{ \frac{x}{\varepsilon} \right\} \in \omega^l_\varepsilon$ and its complement pore $\Pi^l_\varepsilon := Y^l_\varepsilon \setminus \overline{\omega^l_\varepsilon}$ which are separated by the local interface $\partial\omega^l_\varepsilon$ with the normal ν same as for $\partial\omega$. Gathering over all $l \in I^\varepsilon$ we define the disconnected domain of periodic particles (the solid phase) $\omega_\varepsilon := \bigcup_{l \in I^\varepsilon} \omega^l_\varepsilon$ and its connected complement $\Pi_\varepsilon := \Omega_\varepsilon \setminus \overline{\omega}_\varepsilon$ which are separated by the union $\partial\omega_\varepsilon := \bigcup_{l \in I^\varepsilon} \partial\omega^l_\varepsilon$. Adding a thin layer $\Omega \setminus \Omega_\varepsilon$ possibly attached to the external boundary $\partial\Omega$ composes the perforated domain (the pore phase) $Q_\varepsilon := (\Omega \setminus \Omega_\varepsilon) \cup \Pi_\varepsilon$.

Given in the two-phase domain functions allow discontinuity across the interface. In the unit cell Y we distinguish the negative face $\partial\omega^-$ as the particle boundary, and the positive face $\partial\omega^+$ as the opposite part of the pore boundary. Then the interface jump of a discontinuous $u(y)$ for $y \in \Pi \cup \omega$ in the unit cell is defined as $[\![u]\!]_y := u|_{\partial\omega^+} - u|_{\partial\omega^-}$, see [6, Section 1.4]. Similarly, gathering over all local cells establishes the positive and negative faces $\partial\omega^\pm_\varepsilon = \bigcup_{l \in I^\varepsilon} (\partial\omega^l_\varepsilon)^\pm$ and the jump of a discontinuous function $f(x)$ for $x \in Q_\varepsilon \cup \omega_\varepsilon$ across the interface $\partial\omega_\varepsilon$ by $[\![f]\!] := f|_{\partial\omega^+_\varepsilon} - f|_{\partial\omega^-_\varepsilon}$.

For the fixed parameter $\varepsilon > 0$, the species with specific charges z_i, molar masses $m_i > 0$, volume factors $\beta_i > 0$, and unknown concentrations $c^\varepsilon_i(t,x)$ for $i = 1, \dots, n$ (where $n \geqslant 2$) are looked together with the overall electrostatic potential $\varphi^\varepsilon(t,x)$ in dependence of $(t,x) \in (0,\tau) \times (Q_\varepsilon \cup \omega_\varepsilon)$, where the final time $\tau > 0$. We formulate the generalized Poisson–Nernst–Planck system following [2]: the Fick's law of diffusion for the flux vectors $J^\varepsilon_i(t,x)$:

$$\frac{\partial c^\varepsilon_i}{\partial t} = \operatorname{div}(J^\varepsilon_i)^\top, \quad (J^\varepsilon_i)^\top = \sum_{j=1}^n c^\varepsilon_j \Big(\nabla \mu^\varepsilon_j - 1_{Q_\varepsilon} \frac{\varepsilon\eta}{N_A C} \Delta v^\varepsilon \Big)^\top m_i D^{ij}_\varepsilon; \tag{1}$$

the electro-chemical potentials:

$$\mu^\varepsilon_i = k_{\mathrm{B}} \Theta \ln(\beta_i c^\varepsilon_i) + 1_{Q_\varepsilon} \frac{\varepsilon}{N_A} \Big(\frac{1}{C} p^\varepsilon + z_i \varphi^\varepsilon \Big); \tag{2}$$

the Stokes flow in pores:

$$-\eta \Delta v^\varepsilon + \nabla p^\varepsilon = -\Big(\sum_{j=1}^n z_j c^\varepsilon_j \Big) \nabla \varphi^\varepsilon, \quad \operatorname{div} v^\varepsilon = 0; \tag{3}$$

and the Gauss's flux law:

$$-\operatorname{div}\Big((\nabla \varphi^\varepsilon)^\top A_\varepsilon \Big) = 1_{Q_\varepsilon} \sum_{j=1}^n z_j c^\varepsilon_j. \tag{4}$$

The equations (1)–(4) contain the indicator function 1_{Q_ε} which is equal to one in Q_ε and zero in ω_ε, the Boltzmann constant k_{B}, the temperature Θ, the Avogadro constant N_A, and the unknown entropy variables implying electro-chemical potentials $\boldsymbol{\mu}^\varepsilon = (\mu^\varepsilon_1, \dots, \mu^\varepsilon_n)(t,x)$, the flow velocity vector $v^\varepsilon = (v^\varepsilon_1, \dots, v^\varepsilon_d)(t,x)$ with the viscosity η, and the pressure $p^\varepsilon(t,x)$. The oscillating matrices $D^{ij}_\varepsilon(x) := D^{ij}\Big(\left\{ \frac{x}{\varepsilon} \right\}\Big)$ and $A_\varepsilon(x) := A\Big(\left\{ \frac{x}{\varepsilon} \right\}\Big)$ are periodic in Ω_ε. The d-by-d matrices $A(y)$ and $D^{ij}(y)$, $i,j = 1, \dots, n$, for $y \in \Pi \cup \omega$ implying the electric permittivity and diffusivity may be discontinuous in the two-phase unit cell and should be uniformly bounded and elliptic.

The constant $C > 0$ stands for summary concentration. For physical consistency, species concentrations should satisfy the total mass balance and positivity conditions (the Gibbs simplex) in the pores:

$$\sum_{i=1}^{n} c_i^\varepsilon = C, \quad c_i^\varepsilon > 0 \ \text{ for } i = 1, \dots, n \quad \text{in } (0, \tau) \times Q_\varepsilon. \tag{5}$$

The parabolic equations (1) are supported by the standard initial condition:

$$c_i^\varepsilon = c_i^{\text{in}} \quad \text{in } Q_\varepsilon \cup \omega_\varepsilon, \tag{6}$$

where the initial data $c_i^{\text{in}} \in H^1(\Omega)$ satisfy the relations in the manner of (5) in Ω.

Lemma 1 (Flux balance) *The constraint (5) and the assumption on the initial data follow* $\sum_{i=1}^n c_i^\varepsilon = \sum_{i=1}^n c_i^{\text{in}} = C$, *hence balance of the total mass* $\frac{\partial}{\partial t}\Big(\sum_{i=1}^n c_i^\varepsilon\Big) = 0$ *holds. If diffusivity matrices are column quasi-stochastic such that*

$$\textstyle\sum_{i=1}^n m_i D^{ij}(y) = \tilde{D}(y) \quad \text{for } j = 1, \dots, n \tag{7}$$

with a uniformly symmetric and elliptic d-by-d matrix $\tilde{D}(y)$ *for* $y \in \Pi \cup \omega$, *then the flux balance* $\sum_{i=1}^n (J_i^\varepsilon)^\top = 0$ *holds.*

Indeed, inserting (2), (3), and (7) into (1) and summing over $i = 1, \dots, n$ it follows (where $\tilde{D}_\varepsilon(x) := \tilde{D}\Big(\Big\{\frac{x}{\varepsilon}\Big\}\Big)$)

$$\sum_{j=1}^{n} c_j^\varepsilon\Big(\nabla \mu_j^\varepsilon - 1_{Q_\varepsilon}\frac{\varepsilon\eta}{N_A C}\Delta \nu^\varepsilon\Big)^\top \tilde{D}_\varepsilon = \Big\{k_B\Theta \sum_{j=1}^{n} \nabla c_j^\varepsilon + 1_{Q_\varepsilon}\frac{\varepsilon}{N_A}\Big(\frac{1}{C}\Big(\sum_{j=1}^{n} c_j^\varepsilon\Big)\nabla p^\varepsilon + \Big(\sum_{j=1}^{n} z_j c_j^\varepsilon\Big)\nabla \varphi^\varepsilon - \frac{\eta}{C}\Big(\sum_{j=1}^{n} c_j^\varepsilon\Big)\Delta \nu^\varepsilon\Big)\Big\}^\top \tilde{D}_\varepsilon = 0.$$

On the outer boundary (the bath boundary) there are supposed the standard Dirichlet boundary conditions:

$$c_i^\varepsilon = c_i^{\text{D}} \ \text{ for } i = 1, \dots, n, \quad \varphi^\varepsilon = \varphi^{\text{D}} \quad \text{on } (0, \tau) \times \partial\Omega, \tag{8}$$

where the Dirichlet data $c_i^{\text{D}} \in H^1(0, \tau; L^2(\Omega)) \cap L^2(0, \tau; H^1(\Omega))$ and $\varphi^{\text{D}} \in L^\infty(0, \tau; H^1(\Omega))$ satisfy similar to (5) relations on $(0, \tau) \times \partial\Omega$ and the compatibility with c_i^{in} at $t = 0$. The important part of modelling is the interface conditions:

$$[\![(J_i^\varepsilon)^\top]\!]\nu = 0, \quad -(J_i^\varepsilon)^\top \nu = \varepsilon^2 g_i(\hat{\mathbf{c}}^\varepsilon, \hat{\varphi}^\varepsilon), \quad [\![(\nabla\varphi^\varepsilon)^\top A_\varepsilon]\!]\nu = 0, \quad -(\nabla\varphi^\varepsilon)^\top A_\varepsilon \nu + \frac{\alpha}{\varepsilon}[\![\varphi^\varepsilon]\!] = g_\varepsilon \quad \text{on } (0, \tau) \times \partial\omega_\varepsilon. \tag{9}$$

In (9), the notation $\hat{\mathbf{c}}^\varepsilon := (\mathbf{c}^\varepsilon|_{\partial\omega_\varepsilon^+}, \mathbf{c}^\varepsilon|_{\partial\omega_\varepsilon^-})$ and $\hat{\varphi}^\varepsilon := (\varphi^\varepsilon|_{\partial\omega_\varepsilon^+}, \varphi^\varepsilon|_{\partial\omega_\varepsilon^-})$ implies the pair of traces at the phase interface $\partial\omega_\varepsilon$. The function $g(y) \in L^\infty(0, \tau; L^2(\partial\omega))$ denotes the electric current through the interface in the unit cell, and $g_\varepsilon(x) := g\Big(\Big\{\frac{x}{\varepsilon}\Big\}\Big)$ is periodic at $\partial\omega_\varepsilon$. The capacitance density $\alpha > 0$. The functions $(\hat{\mathbf{c}}, \hat{\varphi}) \mapsto g_i$, $\mathbb{R}^{2n} \times \mathbb{R}^2 \mapsto \mathbb{R}$, $i = 1, \dots, n$, describe interface fluxes of species with respect to the pair of traces $\hat{\mathbf{c}}$ and $\hat{\varphi}$, they should satisfy the assumptions of balance of mass, positive production rate, and uniform boundedness, respectively:

$$\sum_{i=1}^{n} g_i(\hat{\mathbf{c}}, \hat{\varphi}) = 0; \quad g_i(\hat{\mathbf{c}}, \hat{\varphi}) \cdot \min(0, c_i|_{\partial\omega_\varepsilon^+}) = 0 \text{ on } \partial\omega_\varepsilon^+; \quad |g_i(\hat{\mathbf{c}}, \hat{\varphi})|^2 \leqslant K_{\text{g}}, \quad K_{\text{g}} > 0. \tag{10}$$

A weak formulation of the generalized PNP problem reads: Find $\mathbf{c}^\varepsilon = (c_1^\varepsilon, \dots, c_n^\varepsilon)$ and φ^ε such that

$$c_i^\varepsilon \in L^\infty(0, \tau; L^2(Q_\varepsilon) \times L^2(\omega_\varepsilon)) \cap L^2(0, \tau; H^1(Q_\varepsilon) \times H^1(\omega_\varepsilon)), \quad \varphi^\varepsilon \in L^\infty(0, \tau; H^1(Q_\varepsilon) \times H^1(\omega_\varepsilon)), \tag{11}$$

which satisfy the Dirichlet boundary conditions (8), the initial conditions (6), the total mass balance and positivity conditions (5), and fulfill the variational equations (for $i = 1, \dots, n$):

$$\int_0^\tau\!\!\int_{Q_\varepsilon \cup \omega_\varepsilon} \Big\{\frac{\partial c_i^\varepsilon}{\partial t}\bar{c}_i + \sum_{j=1}^{n}\Big[k_B\Theta\nabla c_j^\varepsilon + \varepsilon 1_{Q_\varepsilon}\Upsilon_j(\mathbf{c}^\varepsilon)\nabla\varphi^\varepsilon\Big]^\top m_i D_\varepsilon^{ij}\nabla\bar{c}_i\Big\}\,dx\,dt = \int_0^\tau\!\!\int_{\partial\omega_\varepsilon} \varepsilon^2 g_i(\hat{\mathbf{c}}^\varepsilon, \hat{\varphi}^\varepsilon)[\![\bar{c}_i]\!]\,dS_x\,dt, \tag{12}$$

$$\int_{Q_\varepsilon \cup \omega_\varepsilon} \Big((\nabla\varphi^\varepsilon)^\top A_\varepsilon \nabla\bar{\varphi} - 1_{Q_\varepsilon}\Big(\sum_{k=1}^{n} z_k c_k^\varepsilon\Big)\bar{\varphi}\Big)\,dx + \frac{\alpha}{\varepsilon}\int_{\partial\omega_\varepsilon} [\![\varphi^\varepsilon]\!][\![\bar{\varphi}]\!]\,dS_x = \int_{\partial\omega_\varepsilon} g_\varepsilon[\![\bar{\varphi}]\!]\,dS_x, \quad t \in (0, \tau), \tag{13}$$

for all test functions $\bar{c}_i \in H^1(0,\tau; L^2(Q_\varepsilon) \times L^2(\omega_\varepsilon)) \cap L^2(0,\tau; H^1(Q_\varepsilon) \times H^1(\omega_\varepsilon))$ and $\bar{\varphi} \in H^1(Q_\varepsilon) \times H^1(\omega_\varepsilon)$ such that $\bar{c}_i = 0$ on $(0,\tau) \times \partial\Omega$ and $\bar{\varphi} = 0$ on $\partial\Omega$. In (12) the time-derivative $\frac{\partial c_i^\varepsilon}{\partial t}$ is understood in the sense of distribution, and the following notation of Lipschitz continuous functions $\Upsilon_j : \mathbb{R}^n \mapsto \mathbb{R}$, $j = 1, \dots, n$, was used for short:

$$\Upsilon_j(\mathbf{c}) := \frac{c_j}{N_A}\Big(z_j - \frac{1}{C}\sum_{k=1}^{n} z_k c_k\Big). \tag{14}$$

Theorem 1 (Well-posedness [7, 8]) *(i) Under all the assumptions, there exists a solution (11) of the generalized Poisson–Nernst–Planck problem (12), (13) satisfying the total mass balance in (5). The positivity in (5) is guaranteed locally at least for small $\tau(\varepsilon) \geq \tau_0 > 0$. Moreover, if stronger than (7) assumption (implying the decoupling)*

$$m_i D^{ij} = \delta_{ij}\tilde{D}, \quad i, j = 1, \dots, n,$$

is imposed, then the non-negativity $c_i^\varepsilon \geqslant 0$ is guaranteed globally for all $\tau > 0$.

(ii) The solution satisfies the following a-priori estimates, which are uniform in $\varepsilon \in (0, \varepsilon_0)$, with $K_\varphi, \gamma_c, K_c > 0$:

$$|||\boldsymbol{c}^\varepsilon|||^2 := \|\boldsymbol{c}^\varepsilon\|^2_{L^\infty(0,\tau;L^2(Q_\varepsilon)\times L^2(\omega_\varepsilon))} + \|\boldsymbol{c}^\varepsilon\|^2_{L^2(0,\tau;H^1(Q_\varepsilon)\times H^1(\omega_\varepsilon))} \leqslant K_c + \gamma_c K_\varphi, \quad \|\varphi^\varepsilon\|^2_{L^\infty(0,\tau;H^1(Q_\varepsilon)\times H^1(\omega_\varepsilon))} \leqslant K_\varphi. \tag{15}$$

HOMOGENIZATION OF THE PROBLEM

For homogenization of the periodic function g and periodic matrices A and D, three auxiliary problems are formulated in the two-phase unit cell $\Pi \cup \omega$. First, for the interface electric current g we set the cell problem to find $\Lambda(y)$:

$$-\mathrm{div}_y\Big((\nabla_y\Lambda)^\top A\Big) = 0 \quad \text{in } \Pi \cup \omega; \quad [\![(\nabla_y\Lambda)^\top A]\!]_y \nu = 0, \quad -(\nabla_y\Lambda)^\top A\nu + \alpha[\![\Lambda]\!]_y = g \quad \text{on } \partial\omega; \tag{16}$$

satisfying the periodicity conditions: $(\nabla_y\Lambda)^\top A_{(\cdot,k)}\big|_{y_k=0} = (\nabla_y\Lambda)^\top A_{(\cdot,k)}\big|_{y_k=1}$, $\Lambda|_{y_k=0} = \Lambda|_{y_k=1}$ for $k = 1, \dots, d$. Based on the standard elliptic theory, in the space of periodic functions $H^1_\#(\Pi) = \{u \in H^1(\Pi) : u|_{y_k=0} = u|_{y_k=1},\ k = 1, \dots, d\}$ there exists a variational solution $\Lambda \in H^1_\#(\Pi) \times H^1(\omega)$ of the problem (16) such that

$$\int_{\Pi\cup\omega} (\nabla_y\Lambda)^\top A\, \nabla_y u\, dy + \int_{\partial\omega} \alpha[\![\Lambda]\!]_y [\![u]\!]_y\, dS_y = \int_{\partial\omega} g[\![u]\!]_y\, dS_y \tag{17}$$

for all test functions $u \in H^1_\#(\Pi) \times H^1(\omega)$, which is defined up to a constant value in the cell Y.

Second, for the permittivity matrix $A(y)$ we formulate the following boundary value problem for a vector-function $\Phi = (\Phi_1, \dots, \Phi_d)(y)$ in the two-phase unit cell:

$$-\mathrm{div}_y\Big((\partial_y\Phi + I)A\Big) = 0 \quad \text{in } \Pi \cup \omega; \quad [\![(\partial_y\Phi + I)A]\!]_y \nu = 0, \quad -(\partial_y\Phi + I)A\nu + \alpha[\![\Phi]\!]_y = 0 \quad \text{on } \partial\omega; \tag{18}$$

satisfying the periodicity conditions: $(\partial_y\Phi + I)A_{(\cdot,k)}\big|_{y_k=0} = (\partial_y\Phi + I)A_{(\cdot,k)}\big|_{y_k=1}$, $\Phi|_{y_k=0} = \Phi|_{y_k=1}$ for $k = 1, \dots, d$. In (18), the divergence is taken for every $\Phi_i(y)$, the notation $\partial_y\Phi(y)$ for $y \in \Pi \cup \omega$ stands for the $d \times d$-matrix of derivatives, and I is the $d \times d$-identity matrix. The weak form of (18) implies: Find $\Phi \in (H^1_\#(\Pi) \times H^1(\omega))^d$ such that

$$\int_{\Pi\cup\omega} (\partial_y\Phi + I)A\nabla_y u\, dy + \int_{\partial\omega} \alpha[\![\Phi]\!]_y [\![u]\!]_y\, dS_y = 0 \tag{19}$$

for all test functions $u \in H^1_\#(\Pi) \times H^1(\omega)$. A solution Φ to (19) exists up to a constant in the cell Y.

Third, for a diffusivity matrix D, in analogy with (18) we establish the cell problem for $N = (N_1, \dots, N_d)(y)$:

$$-\mathrm{div}_y\Big((\partial_y N + I)D\Big) = 0 \quad \text{in } \Pi \cup \omega; \quad [\![(\partial_y N + I)D]\!]_y \nu = 0, \quad -(\partial_y N + I)D\nu = 0 \quad \text{on } \partial\omega; \tag{20}$$

satisfying the periodicity conditions: $(\partial_y N + I)D_{(\cdot,k)}\big|_{y_k=0} = (\partial_y N + I)D_{(\cdot,k)}\big|_{y_k=1}$, $N|_{y_k=0} = N|_{y_k=1}$ for $k = 1, \dots, d$. The system (20) differs from (18) by the interface condition and possesses the variational solution $N \in (H^1_\#(\Pi) \times H^1(\omega))^d$ defined up to a piecewise constant in $\Pi \cup \omega$ such that

$$\int_{\Pi\cup\omega} (\partial_y N + I)D\nabla_y u\, dy = 0 \tag{21}$$

for all test functions $u \in H^1_\#(\Pi) \times H^1(\omega)$. Since $\overline{\omega} \subset Y$ is isolated, then $N = -y$ and $\partial_y N = -I$ in ω.

We assume that the diffusivity matrices D^{ij} admit the asymptotic decomposition as follows

$$m_i D^{ij}(y) = \delta_{ij} D(y) + \varepsilon \tilde{D}^{ij}(y) \quad \text{for } y \in \Pi \cup \omega, \tag{22}$$

with d-by-d matrices $\tilde{D}^{ij}$, $i, j = 1, \ldots, n$ and a d-by-d uniformly bounded, symmetric positive definite matrix D. With the help of assumption (22) we establish the averaged PNP equations for $(\mathbf{c}^0, \varphi^0)(t, x)$ (where the porosity $\varkappa = \frac{|\Pi|}{|Y|}$):

$$\frac{\partial c_i^0}{\partial t} - \operatorname{div}\Big(k_{\mathrm{B}}\Theta(\nabla c_i^0)^\top D^0\Big) = 0 \quad \text{for } i = 1, \ldots, n; \quad -\operatorname{div}\Big((\nabla\varphi^0)^\top A^0\Big) = \varkappa \sum_{k=1}^n z_k c_k^0 \quad \text{in } (0,\tau) \times \Omega, \tag{23}$$

which are supported by the standard Dirichlet boundary and initial conditions:

$$c_i^0 = c_i^{\mathrm{D}} \quad \text{and} \quad \varphi^0 = \varphi^{\mathrm{D}} \quad \text{on } (0,\tau) \times \partial\Omega; \quad c_i^0 = c_i^{\mathrm{in}} \quad \text{in } \Omega. \tag{24}$$

In (23), the averaged matrices

$$A^0 = \langle (\partial_y \Phi + I)\, A \rangle_{\Pi\cup\omega}, \quad D^0 = \langle (\partial_y N + I)\, D \rangle_{\Pi}$$

for D from (22), the vectors Φ and N are the solutions of the two-phase cell problems (19) and (21), respectively. From the standard existence theorems on elliptic and parabolic systems, the solution $\varphi^0 \in L^\infty(0,\tau; H^1(\Omega))$ and $c_i^0 \in L^\infty(0,\tau; L^2(\Omega)) \cap L^2(0,\tau; H^1(\Omega))$ of the linear problem (23) exists and fulfills the following variational equations:

$$\int_0^\tau\!\!\int_\Omega \Big\{ \frac{\partial c_i^0}{\partial t} \bar{c}_i + k_{\mathrm{B}}\Theta(\nabla c_i^0)^\top D^0 \nabla \bar{c}_i \Big\}\, dx\, dt = 0 \quad \text{for } i = 1, \ldots, n; \quad \int_\Omega \Big\{ (\nabla\varphi^0)^\top A^0 \nabla\bar{\varphi} - \varkappa\Big(\sum_{k=1}^n z_k c_k^0\Big)\bar{\varphi} \Big\}\, dx = 0 \tag{25}$$

for all test functions $\bar{c}_i \in H^1(0,\tau; L^2(\Omega)) \cap L^2(0,\tau; H^1_0(\Omega))$ and $\bar{\varphi} \in H^1_0(\Omega)$.

For the further use of the periodic unfolding technique we introduce two linear continuous operators [15]: the two-scale unfolding operator $f(x) \mapsto T_\varepsilon : H^1(Q_\varepsilon) \times H^1(\omega_\varepsilon) \mapsto L^2(\Omega; H^1(\Pi) \times H^1(\omega))$ defined by

$$(T_\varepsilon f)(x, y) = \begin{cases} f\Big(\varepsilon\lfloor \frac{x}{\varepsilon} \rfloor + \varepsilon y\Big), & \text{a.e. for } x \in \Omega_\varepsilon \\ f(x), & \text{a.e. for } x \in \Omega \setminus \Omega_\varepsilon \end{cases} \quad \text{and } y \in \Pi \cup \omega, \tag{26}$$

and its left-inverse operator $u(x, y) \mapsto T_\varepsilon^{-1} : L^2(\Omega; H^1(\Pi) \times H^1(\omega)) \mapsto H^1(\bigcup_{l \in I^\varepsilon} \Pi_\varepsilon^l) \times H^1(\omega_\varepsilon) \times H^1(\Omega \setminus \Omega_\varepsilon)$ called the two-scale averaging operator (which is discontinuous across ∂Y_ε^l and $\partial\Omega_\varepsilon$) by

$$(T_\varepsilon^{-1} u)(x) = \begin{cases} \dfrac{1}{|Y|} \displaystyle\int_{\Pi\cup\omega} u\Big(\varepsilon\lfloor \frac{x}{\varepsilon} \rfloor + \varepsilon z, \Big\{\frac{x}{\varepsilon}\Big\}\Big)\, dz, & \text{a.e. for } x \in \Pi_\varepsilon \cup \omega_\varepsilon, \\ \dfrac{1}{|Y|} \displaystyle\int_{\Pi\cup\omega} u(x, y)\, dy, & \text{a.e. for } x \in \Omega \setminus \Omega_\varepsilon. \end{cases} \tag{27}$$

Theorem 2 (Averaged problem and correctors [14]) *Let the solutions Φ, N of the two-phase cell problems (19), (21), and $\partial_y\Phi$, $\partial_y N$ be uniformly bounded in $\Pi \cup \omega$, the averaged solutions $\varphi^0 \in L^\infty(0,\tau; H^3(\Omega))$ and $c_i^0 \in L^2(0,\tau; H^3(\Omega))$, $i = 1, \ldots, n$. Then solutions $(\boldsymbol{c}^\varepsilon, \varphi^\varepsilon)$ of the inhomogeneous PNP problem (12), (13) and the solution $(\boldsymbol{c}^0, \varphi^0)$ of the homogenized mono-domain PNP problem (25) satisfy the residual error estimates:*

$$|||\boldsymbol{c}^\varepsilon - \boldsymbol{c}^1|||^2 \le \varepsilon K_c^1, \quad \|\varphi^\varepsilon - \varphi^2\|^2_{L^\infty(0,\tau; H^1(Q_\varepsilon) \times H^1(\omega_\varepsilon))} \le \varepsilon K_\varphi^1 \quad (K_c^1, K_\varphi^1 > 0), \tag{28}$$

with the norm $|||\cdot|||$ defined in (15), and the correctors are

$$c_i^1 := c_i^0 + \varepsilon(\nabla c_i^0)^\top (T_\varepsilon^{-1} N)\eta_{\Omega_\varepsilon}, \quad \varphi^2 := \varphi^1 + \varepsilon(T_\varepsilon^{-1}\Lambda)\eta_{\Omega_\varepsilon}, \quad \varphi^1 := \varphi^0 + \varepsilon(\nabla\varphi^0)^\top (T_\varepsilon^{-1}\Phi)\eta_{\Omega_\varepsilon}. \tag{29}$$

In (29), the vector Λ is a solution of the two-phase cell problem (17), and $\eta_{\Omega_\varepsilon}$ is a smooth cut-off function supported in Ω_ε and equals one outside an ε-neighborhood of $\partial\Omega_\varepsilon$.

CORRECTOR DUE TO NONLINEAR INTERFACE CONDITION

We set the fourth auxiliary two-phase cell problem for $\Xi(y)$:

$$-\mathrm{div}_y\Big((\nabla_y\Xi)^\top D\Big) + \Xi = 0 \quad \text{in } \Pi\cup\omega; \quad [\![(\nabla_y\Xi)^\top D]\!]_y\nu = 0, \quad -(\nabla_y\Xi)^\top D\nu = 1 \quad \text{on } \partial\omega; \tag{30}$$

satisfying the periodicity conditions: $(\nabla_y\Xi)^\top D_{(\cdot,k)}|_{y_k=0} = (\nabla_y\Xi)^\top D_{(\cdot,k)}|_{y_k=1}$, $\Xi|_{y_k=0} = \Xi|_{y_k=1}$ for $k = 1,\dots,d$. It possesses the unique variational solution $\Xi \in H^1_\#(\Pi)\times H^1(\omega)$ such that for all periodic test functions $u \in H^1_\#(\Pi)\times H^1(\omega)$:

$$\int_{\Pi\cup\omega}\Big((\nabla_y\Xi)^\top D\nabla_y u + \Xi u\Big)\,dy = \int_{\partial\omega}[\![u]\!]_y\,dS_y. \tag{31}$$

Now we average the interface data, which are not periodic, by using (31) and introducing the corrector

$$c_i^2 := c_i^1 + \varepsilon\chi_i + \varepsilon^2(\nabla\chi_i)^\top(T_\varepsilon^{-1}N)\eta_{\Omega_\varepsilon}, \quad i = 1,\dots,n, \tag{32}$$

with the help of linear diffusion equations for $\chi_i(t,x)$, $i = 1,\dots,n$:

$$\frac{\partial\chi_i}{\partial t} - \mathrm{div}\Big(k_\mathrm{B}\Theta(\nabla\chi_i)^\top D^0\Big) = \varepsilon\langle G_i\rangle_{\partial\omega_\varepsilon}(T_\varepsilon^{-1}\Xi) \quad \text{in } (0,\tau)\times\Omega, \tag{33}$$

supported by the homogeneous interface, boundary, and initial conditions:

$$[\![\chi_i]\!] = 0,\ -k_\mathrm{B}\Theta[\![\nabla\chi_i]\!]^\top D^0\nu = 0 \quad \text{on } (0,\tau)\times\partial\omega_\varepsilon; \quad \chi_i = 0 \quad \text{on } (0,\tau)\times\partial\Omega, \quad \chi_i(0,\cdot) = 0 \quad \text{in } \Omega. \tag{34}$$

The right-hand side in (33) involves piecewise-constant average $\langle G_i\rangle_{\partial\omega_\varepsilon}(t) := \frac{1}{|\partial\omega_\varepsilon|}\int_{\partial\omega_\varepsilon} G_i\,dS_x$ of $G_i(t,x) := g_i(\hat{\mathbf{c}}^0,\hat\varphi^0)$.

Similarly to (25), a variational solution $\chi_i \in L^\infty(0,\tau;L^2(\Omega))\cap L^2(0,\tau;H^1(\Omega))$ exists and $\boldsymbol{\chi} = (\chi_1,\dots,\chi_n)$ satisfies

$$\int_0^\tau\!\!\int_\Omega\Big\{\frac{\partial\chi_i}{\partial t}\bar c_i + k_\mathrm{B}\Theta(\nabla\chi_i)^\top D^0\nabla\bar c_i\Big\}\,dx\,dt = \int_0^\tau\!\!\int_{Q_\varepsilon\cup\omega_\varepsilon}\varepsilon\langle G_i\rangle_{\partial\omega_\varepsilon}(T_\varepsilon^{-1}\Xi)\bar c_i\,dx\,dt \tag{35}$$

for continuous across $\partial\omega_\varepsilon$ test functions $\bar c_i \in H^1(0,\tau;L^2(\Omega))\cap L^2(0,\tau;H^1_0(\Omega))$. Applying to χ_i Green's formulas separately in Q_ε and ω_ε and using relations (33), (34), in this way we derive the equivalent variational equation:

$$\int_0^\tau\!\!\int_{Q_\varepsilon\cup\omega_\varepsilon}\Big\{\frac{\partial\chi_i}{\partial t}\bar c_i + k_\mathrm{B}\Theta(\nabla\chi_i)^\top D^0\nabla\bar c_i\Big\}\,dx\,dt + \int_0^\tau\!\!\int_{\partial\omega_\varepsilon}k_\mathrm{B}\Theta(\nabla\chi_i)^\top D^0\nu[\![\bar c_i]\!]\,dS_x\,dt = \int_0^\tau\!\!\int_{Q_\varepsilon\cup\omega_\varepsilon}\varepsilon\langle G_i\rangle_{\partial\omega_\varepsilon}(T_\varepsilon^{-1}\Xi)\bar c_i\,dx\,dt \tag{36}$$

for discontinuous across $\partial\omega_\varepsilon$ functions $\bar c_i \in H^1(0,\tau;L^2(Q_\varepsilon)\times L^2(\omega_\varepsilon))\cap L^2(0,\tau;H^1(Q_\varepsilon)\times H^1(\omega_\varepsilon))$ and $\bar c_i = 0$ on $\partial\Omega$.

Lemma 2 (Asymptotic formula for non-periodic interface data) *Assume that the solution of (35) is smooth such that $\chi_i \in L^2(0,\tau;H^3(\Omega))$. For arbitrary functions $\bar c_i \in H^1(0,\tau;L^2(Q_\varepsilon)\times L^2(\omega_\varepsilon))\cap L^2(0,\tau;H^1(Q_\varepsilon)\times H^1(\omega_\varepsilon))$, $i = 1,\dots,n$, the following asymptotic formula holds:*

$$\int_0^\tau\!\!\int_{Q_\varepsilon\cup\omega_\varepsilon}\Big\{\frac{\partial\chi_i}{\partial t}\bar c_i + k_\mathrm{B}\Theta(\nabla\chi_i)^\top D^0\nabla\bar c_i\Big\}\,dx\,dt + \int_0^\tau\!\!\int_{\partial\omega_\varepsilon}k_\mathrm{B}\Theta(\nabla\chi_i)^\top D^0\nu[\![\bar c_i]\!]\,dS_x\,dt = \int_0^\tau\!\!\int_{\partial\omega_\varepsilon}\varepsilon G_i[\![\bar c_i]\!]\,dS_x\,dt + O(\varepsilon). \tag{37}$$

In order to prove Lemma 2 we set auxiliary functions $\Psi_i(y)$, $i = 1,\dots,n$, such that

$$-\mathrm{div}_y\Big((\nabla_y\Psi_i)^\top D\Big) = 0 \quad \text{in } \Pi\cup\omega; \quad [\![(\nabla_y\Psi_i)^\top D]\!]_y\nu = 0, \quad -(\nabla_y\Psi_i)^\top D\nu = T_\varepsilon G_i - \langle T_\varepsilon G_i\rangle_{\partial\omega} \quad \text{on } \partial\omega; \tag{38}$$

satisfying the periodicity conditions: $(\nabla_y\Psi_i)^\top D_{(\cdot,k)}|_{y_k=0} = (\nabla_y\Psi_i)^\top D_{(\cdot,k)}|_{y_k=1}$, $\Psi_i|_{y_k=0} = \Psi_i|_{y_k=1}$ for $k = 1,\dots,d$. The problem (38) has the variational solution $\Psi_i \in H^1_\#(\Pi)\times H^1(\omega)$ defined up to a piecewise constant in $\Pi\cup\omega$ such that

$$\int_{\Pi\cup\omega}(\nabla_y\Psi_i)^\top D\nabla_y u\,dy = \int_{\partial\omega}(T_\varepsilon G_i - \langle T_\varepsilon G_i\rangle_{\partial\omega})[\![u]\!]_y\,dS_y \tag{39}$$

for all test functions $u \in H^1_\#(\Pi)\times H^1(\omega)$. We note that the solvability condition $\int_{\partial\omega}(T_\varepsilon G_i - \langle T_\varepsilon G_i\rangle_{\partial\omega})\,dS_y = 0$ holds for the Neumann problem (39), and $T_\varepsilon G_i$ is bounded uniform in ε in virtue of assumptions (10) on $g_i(\cdot,\cdot)$.

Multiplying the equation (31) with $\langle T_\varepsilon G_i\rangle_{\partial\omega}$ and summing it with the equation (39) for Ψ_i leads to

$$\int_{\partial\omega} T_\varepsilon G_i [\![u]\!]_y \, dS_y = \int_{\Pi\cup\omega} \Big((\nabla_y(\langle T_\varepsilon G_i\rangle_{\partial\omega}\Xi) + \Psi_i)^\top D\nabla_y u + \langle T_\varepsilon G_i\rangle_{\partial\omega}\Xi u \Big)\, dy.$$

We integrate it over Ω_ε, multiply with $\frac{1}{|Y|}$, test with $T_\varepsilon^{-1}u = \bar{c}_i$, and apply the two-scale integration rules [15]:

$$\frac{1}{|Y|}\int_{\Omega_\varepsilon}\int_{\partial\omega} T_\varepsilon G_i[\![u]\!]_y\, dS_y\, dx = \int_{\partial\omega_\varepsilon} \varepsilon G_i[\![\bar{c}_i]\!]\, dS_x, \quad \frac{1}{|Y|}\int_{\Omega_\varepsilon}\int_{\Pi\cup\omega} \langle T_\varepsilon G_i\rangle_{\partial\omega}\Xi u\, dy\, dx = \int_{Q_\varepsilon\cup\omega_\varepsilon} \varepsilon\langle G_i\rangle_{\partial\omega_\varepsilon}(T_\varepsilon^{-1}\Xi)\bar{c}_i\, dx,$$

$$\frac{1}{|Y|}\int_{\Omega_\varepsilon}\int_{\Pi\cup\omega} (\nabla_y(\langle T_\varepsilon G_i\rangle_{\partial\omega}\Xi) + \Psi_i)^\top D\nabla_y u\, dy = \int_{Q_\varepsilon\cup\omega_\varepsilon} \varepsilon^2\Big[\nabla(\langle G_i\rangle_{\partial\omega_\varepsilon}(T_\varepsilon^{-1}\Xi)) + (T_\varepsilon^{-1}\Psi_i)\Big]^\top (T_\varepsilon^{-1}D)\nabla\bar{c}_i\, dx,$$

then use $\langle G_i\rangle_{\partial\omega_\varepsilon} = O(\varepsilon^{-1})$, the boundedness assumption (10), and $|\partial\omega_\varepsilon| = O(\varepsilon^{-1})$ to conclude that

$$\int_{\partial\omega_\varepsilon} \varepsilon G_i[\![\bar{c}_i]\!]\, dS_x = \int_{Q_\varepsilon\cup\omega_\varepsilon} \varepsilon\langle G_i\rangle_{\partial\omega_\varepsilon}(T_\varepsilon^{-1}\Xi)\bar{c}_i\, dx + O(\varepsilon). \tag{40}$$

Inserting (40) in (36) it follows (37) thus proving the lemma.

Theorem 3 (Non-periodic interface corrector) *Let the assumptions of Theorem 2 hold, the solution of problem (35) possess $\chi_i \in L^2(0,\tau; H^3(\Omega))$, and g_i be Lipschitz continuous such that*

$$|g_i(\hat{\boldsymbol{c}}^\varepsilon, \hat{\varphi}^\varepsilon) - g_i(\hat{\boldsymbol{c}}^2, \hat{\varphi}^2)|^2 \le K_{\rm L}|\hat{\boldsymbol{c}}^\varepsilon - \hat{\boldsymbol{c}}^2|^2 + K_{\rm M}|\hat{\varphi}^\varepsilon - \hat{\varphi}^2|^2, \quad K_{\rm L}, K_{\rm M} > 0. \tag{41}$$

Then the solutions $\boldsymbol{c}^\varepsilon$ and $\boldsymbol{c}^0$ corresponding to the inhomogeneous PNP problem (12), (13), and the homogenized mono-domain PNP problem (25) satisfy the refined residual error estimate (where $\boldsymbol{c}^1$ is from (29) and $\boldsymbol{c}^2$ from (32)):

$$|||\boldsymbol{c}^\varepsilon - \boldsymbol{c}^2|||^2 = O(\varepsilon). \tag{42}$$

The asymptotic formula for periodic interface data [14] applied to χ_i reads:

$$\int_{Q_\varepsilon\cup\omega_\varepsilon} (\nabla\chi_i)^\top D^0\nabla\bar{c}_i\, dx + \int_{\partial\omega_\varepsilon} (\nabla\chi_i)^\top D^0\nu[\![\bar{c}_i]\!]\, dS_x = \int_{Q_\varepsilon\cup\omega_\varepsilon} (\nabla\chi_i^1)^\top D_\varepsilon\nabla\bar{c}_i\, dx + O(\varepsilon),$$

where $\chi_i^1 := \chi_i + \varepsilon(\nabla\chi_i)^\top(T_\varepsilon^{-1}N)\eta_{\Omega_\varepsilon} = \chi_i + O(\varepsilon)$. With its help we continue the asymptotic estimate (37) as

$$\int_0^\tau\int_{Q_\varepsilon\cup\omega_\varepsilon} \Big\{\frac{\partial\chi_i}{\partial t}\bar{c}_i + k_{\rm B}\Theta(\nabla\chi_i^1)^\top D_\varepsilon\nabla\bar{c}_i\Big\}\, dx\, dt = \int_0^\tau\int_{\partial\omega_\varepsilon} \varepsilon g_i(\hat{\mathbf{c}}^0, \hat{\varphi}^0)[\![\bar{c}_i]\!]\, dS_x\, dt + O(\varepsilon). \tag{43}$$

The equation (43) for χ_i multiplied by ε, and the following equation for c_i^1 from [14]:

$$\int_0^\tau\int_{Q_\varepsilon\cup\omega_\varepsilon} \Big\{\frac{\partial c_i^1}{\partial t}\bar{c}_i + k_{\rm B}\Theta(\nabla c_i^1)^\top D_\varepsilon\nabla\bar{c}_i\Big\}\, dx\, dt = O(\varepsilon)$$

are subtracted from the equation (12) for c_i^ε, since $\frac{\partial}{\partial t}(c_i^\varepsilon - c_i^2) = \frac{\partial}{\partial t}(c_i^\varepsilon - c_i^1 - \varepsilon\chi_i^1) = \frac{\partial}{\partial t}(c_i^\varepsilon - c_i^1 - \varepsilon\chi_i) + O(\varepsilon^2)$, then

$$\int_0^\tau\int_{Q_\varepsilon\cup\omega_\varepsilon} \Big\{\frac{\partial}{\partial t}(c_i^\varepsilon - c_i^2)\bar{c}_i + k_{\rm B}\Theta(\nabla(c_i^\varepsilon - c_i^2))^\top D_\varepsilon\nabla\bar{c}_i\Big\}\, dx\, dt = I_\varepsilon(\bar{c}_i) + O(\varepsilon). \tag{44}$$

The integral in the right-hand side of (44) implies

$$I_\varepsilon(\bar{c}_i) := \int_0^\tau\int_{\partial\omega_\varepsilon} \varepsilon^2\Big(g_i(\hat{\mathbf{c}}^\varepsilon, \hat{\varphi}^\varepsilon) - g_i(\hat{\mathbf{c}}^0, \hat{\varphi}^0)\Big)[\![\bar{c}_i]\!]\, dS_x\, dt = \int_0^\tau\int_{\partial\omega_\varepsilon} \varepsilon^2\Big(g_i(\hat{\mathbf{c}}^\varepsilon, \hat{\varphi}^\varepsilon) - g_i(\hat{\mathbf{c}}^2, \hat{\varphi}^2)\Big)[\![\bar{c}_i]\!]\, dS_x\, dt + O(\varepsilon)$$

due to the Lipschitz continuity (41) of $g_i(\,\cdot\,,\,\cdot\,)$ and $\mathbf{c}^2 - \mathbf{c}^0 = O(\varepsilon)$, $\varphi^2 - \varphi^0 = O(\varepsilon)$. Using the trace theorem

$$\|\hat{c}_i\|^2_{L^2(\partial\omega_\varepsilon)} \leqslant K_0\Big(\frac{1}{\varepsilon}\|c_i\|^2_{L^2(Q_\varepsilon)\times L^2(\omega_\varepsilon)} + \varepsilon\|\nabla c_i\|^2_{L^2(Q_\varepsilon)\times L^2(\omega_\varepsilon)}\Big) \leqslant \frac{K_0}{\varepsilon}\|c_i\|^2_{H^1(Q_\varepsilon)\times H^1(\omega_\varepsilon)},$$

the term $I_\varepsilon(\bar{c}_i)$ is evaluated by Young's inequality such that

$$I_\varepsilon(\bar{c}_i) = \varepsilon\frac{K_0}{2}\Big(K_{\rm L}\|\mathbf{c}^\varepsilon - \mathbf{c}^2\|^2_{L^2(0,\tau;H^1(Q_\varepsilon)\times H^1(\omega_\varepsilon))} + K_{\rm M}\|\varphi^\varepsilon - \varphi^2\|^2_{L^2(0,\tau;H^1(Q_\varepsilon)\times H^1(\omega_\varepsilon))} + \|\bar{c}_i\|^2_{L^2(0,\tau;H^1(Q_\varepsilon)\times H^1(\omega_\varepsilon))}\Big) + O(\varepsilon).$$

We insert here $\bar{c}_i = c_i^\varepsilon - c_i^2$ and the uniform estimates (28) for $\varphi^\varepsilon - \varphi^2$, after summation resulting in

$$\sum_{i=1}^n I_\varepsilon(c_i^\varepsilon - c_i^2) = \varepsilon K\|\mathbf{c}^\varepsilon - \mathbf{c}^2\|^2_{L^2(0,\tau;H^1(Q_\varepsilon)\times H^1(\omega_\varepsilon))} + O(\varepsilon), \quad K = \frac{1}{2}K_0(nK_{\rm L} + 1). \tag{45}$$

Testing (44) with $\bar{c}_i = c_i^\varepsilon - c_i^2$ which is zero at $\partial\Omega$, integrating by parts over time the first term and using the ellipticity of D_ε with the lower bound $\underline{d} > 0$ for the second term, after summation over $i = 1, \ldots, n$ due to (45) we get

$$\frac{1}{2}\|(\mathbf{c}^\varepsilon - \mathbf{c}^2)\big|_{t=0}^{\tau}\|^2_{L^2(Q_\varepsilon)\times L^2(\omega_\varepsilon)} + (k_{\rm B}\Theta\underline{d} - \varepsilon K)\|\nabla(\mathbf{c}^\varepsilon - \mathbf{c}^2)\|^2_{L^2(0,\tau;L^2(Q_\varepsilon)\times L^2(\omega_\varepsilon))} = \varepsilon K\|\mathbf{c}^\varepsilon - \mathbf{c}^2\|^2_{L^2(0,\tau;L^2(Q_\varepsilon)\times L^2(\omega_\varepsilon))} + O(\varepsilon).$$

Accounting for the smallness $(c_i^\varepsilon - c_i^2)(0) = -\varepsilon(\nabla c_i^{\rm in})^\top(T_\varepsilon^{-1}N)\eta_{\Omega_\varepsilon} - \varepsilon^2(\nabla\chi_i)^\top(T_\varepsilon^{-1}N)\eta_{\Omega_\varepsilon} = O(\varepsilon)$ as $t = 0$ and taking supremum over time, it follows the refined residual error estimate (42).

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