

ELECTRO-KINETIC STRUCTURE MODEL WITH INTERFACIAL REACTIONS

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Summary: *In the framework of fundamentals of smart materials and structures, a proper mathematical modeling of electro-kinetic transport phenomena in micro-structures adhering to the law of conservation of mass is suggested. The reference multiphase medium is described by a nonlinear Poisson–Nernst–Planck model stated in a heterogeneous pore-particle space disjoint by the interface. For physical consistency it allows nonlinear boundary reactions at the phase interface. Based on suitable entropy variables, a variational principle is established within the Gibbs simplex preserving a volume balance and positive concentrations. The resulting generalized model is provided by rigorous analysis and supported by homogenization of stationary states.*

1. INTRODUCTION

From the perspective of mathematical modeling of smart materials and structures, in the present work we consider a multiphase medium consisted of multiple components (chemical substances, or bio-molecular species). It is described by a non-linear system of partial differential equations called the Poisson–Nernst–Planck model. Such models have numerous applications describing electro-kinetic phenomena in electro-chemical and bio-molecular cells, photo-voltaic devices, and semiconductors. Our specific motivation concerns, in particular, Li-Ion batteries (see [1]).

For instance, we bear in mind a solid electrolyte composite in which charged species underlie a purely diffusive process in solid particles as well as diffusion and electro-migration in the surrounding pore space. This requires to account for boundary reactions at the phase interface which are of the primary importance in engineering applications. Although this situation happens for a specific modeling of the electrical double layer, it requires a proper description of interfacial reactions in a broad scope.

In particular, the interface phenomena result in a mathematical difficulty dealing with multiphase problems stated in a discontinuous pore-particle space under transmission boundary conditions allowing jumps. The literature on the corresponding modeling and analysis of transmission problems is rather scarce, e.g. [2, 3, 4]. The principal advance in this respect it attained by employing variational techniques in singular domains, which we refer for instance to [5].

The Poisson–Nernst–Planck equations are widely used for modeling of a multiphase medium in various contexts, see [6, 7, 8]. It is closely related to a broad class of other relevant transport equations in statistical mechanics, e.g. [9, 10, 11, 12], as adopted, for example, in semiconductor physics [13]. One of the important directions of the research here concerns homogenization of fine structures at the micro level to get suitable averaged models at the macro-level. We refer to [14, 15, 16] for suitable methods adopted in the field of asymptotic homogenization and, e.g., to [17, 18] for the related methods of singular perturbations in topology optimization.

The classic Poisson–Nernst–Planck model is currently the subject of various modifications for improving its drawbacks, in particular, preserving the conservation law of mass. Many works in this respect have been done in the WIAS in the group of W. Dreyer and other authors cited in [19]. The successful generalization suggests coupling phenomena between species in the electro-kinetic system and accounting for the pressure according to the incompressible Navier–Stokes equation. The other challenge is to treat physically consistent quantities within Gibbs simplex in appropriate manner. This task suggests alternative approaches like excluded volume models, for example, the Bikerman–Freise, Fermi–Dirac, see its description in [20]. Further development in this direction suggests the Maxwell–Stefan diffusion, see [21].

In the present contribution, based on the general thermodynamic principles, see [22, 23, 24], on the one hand, we introduce in consideration the proper entropy variables: pressure and quasi-Fermi electro-chemical potentials, that agrees with the Dreyer generalization. Moreover, these variables are justified by a suitable variational principle established within the Gibbs simplex, which constrains the mixture components to have a constant summary volume and positive concentrations. In fact, from the optimization viewpoint, the pressure and the quasi-Fermi potentials appear in the model as Lagrange multipliers to the volume balance and the positivity constraints, respectively.

On the other hand, the mathematical formalism suitable for rigorous analysis of the underlying physical models was developed in [25] and other works by T. Roubíček. On its basis, in the present work we construct an equivalent, reduced model without constraints, which satisfies a-posteriori the positivity and volume balance conditions constituting the Gibbs simplex. These conditions are ensured by diffusion fluxes with specific diffusivities, which are related to stochastic matrices, by the positive production rate of boundary reactions and balance of the respective boundary terms.

In this way, employing the reduced model formulation we establish the following results: the weak maximum principle, conservation of mass and volume balance, existence of a weak solution of the problem supported by the energy and entropy estimates, entropy dissipation and uniqueness of the solution in a special case, and formal homogenization of the stationary state.

2. NOTATION

For convenience we collect below the notation used in the following consideration.

- $k_B \approx 1.38e-23$ ($\frac{J}{K}$) Boltzmann constant, positive
- θ (K) absolute temperature, positive and constant
- A ($\frac{F}{m}$) electric permittivity, symmetric positive-definite (spd) matrix
- g ($\frac{C}{m^2}$) electric displacement at boundary
- α ($\frac{F}{m^2}$) capacitance density at boundary, positive
- D^{ij} ($\frac{m^2}{J \cdot s}$) diffusivity matrices, $i, j = 1, \dots, n$
- D ($\frac{m^2}{J \cdot s}$) diffusivity, spd-matrix
- J_i ($\frac{1}{m^2 \cdot s}$) diffusion fluxes of species, $i = 1, \dots, n$
- g_i ($\frac{1}{m^2 \cdot s}$) boundary fluxes of species, $i = 1, \dots, n$
- z_i (C) electric charges of species, $i = 1, \dots, n$, constants
- β_i (m^3) volume factors of species, $i = 1, \dots, n$, positive
- c_i ($\frac{1}{m^3}$) concentrations of species, $i = 1, \dots, n$, positive
- C ($\frac{1}{m^3}$) summary concentration, positive and constant
- μ_i (J) electro-chemical potentials of species, $i = 1, \dots, n$
- ϕ (V) electrostatic potential
- p (Pa) pressure

3. GOVERNING PRINCIPLES

We start with the geometric description of the reference configuration. Let $\Omega \subset \mathbb{R}^d$ be a reference domain (associated to a bath) of the spatial dimension $d \in \{1, 2, 3\}$ with the Lipschitz boundary $\partial\Omega$. With $\nu = (\nu_1, \dots, \nu_d)^\top$ the unit normal vector at the boundary $\partial\Omega$ and outward to Ω is denoted, where the upper $^\top$ stands for transposition swapping columns and rows.

Bearing in mind micro-particles of a small size ε , we split Ω in the solid phase $\omega^\varepsilon \subset \Omega$ and the surrounding pore space $\Omega^\varepsilon = \Omega \setminus \overline{\omega^\varepsilon}$ disjoint by the interface Σ^ε with faces Σ_\pm^ε such that

$$\overline{\Omega} = \Omega^\varepsilon \cup \omega^\varepsilon \cup \Sigma^\varepsilon \cup \partial\Omega, \quad \partial\Omega^\varepsilon \cap \Omega =: \Sigma_+^\varepsilon, \quad \partial\omega^\varepsilon \cap \Omega =: \Sigma_-^\varepsilon. \quad (1)$$

By this, we assume that ω^ε is a domain (which can consist of multiple disconnected parts associating solid particles) of the positive Hausdorff measure $|\omega^\varepsilon| > 0$ with the Lipschitz boundary $\partial\omega^\varepsilon$ and the unit normal vector ν which is outward to ω^ε .

Given n charged species (ions) characterized by the charges z_1, \dots, z_n , we look for an unknown temporal distribution over the multiphase medium of the specie concentrations $\mathbf{c}(t, x)$, $\mathbf{c} = (c_1, \dots, c_n)^\top$, and the overall electrostatic potential $\phi(t, x)$ with respect to the time $t \in \mathbb{R}_+$ and the spatial coordinates $x = (x_1, \dots, x_d)^\top \in \mathbb{R}^d$.

Our modeling is based on the following general principles. First, the Fickian law of diffusion

$$\frac{\partial}{\partial t} c_i = \operatorname{div} J_i, \quad i = 1, \dots, n \quad (2a)$$

employs the vector-valued diffusion fluxes $J_i(t, x)$ which are determined by the constitutive law

$$J_i = \sum_{j=1}^n c_j \nabla \mu_j^\top D^{ij}, \quad i = 1, \dots, n, \quad D^{ij} \in \mathbb{R}^{d \times d} \quad (2b)$$

for the electro-chemical potentials $\boldsymbol{\mu}(t, x)$, $\boldsymbol{\mu} = (\mu_1, \dots, \mu_n)^\top$, with the diffusivity d -by- d matrices D^{ij} , $i, j = 1, \dots, n$. Here and in what follows div stands for the divergence, and ∇ for the gradient. The fluxes have to fulfill the balance equation implying the conservation of mass:

$$\sum_{i=1}^n J_i = 0. \quad (2c)$$

Second, the specie concentrations are physically consistent within a Gibbs simplex requiring the positivity and the volume balance condition preserving a summary concentration $C > 0$:

$$c_i > 0, \quad i = 1, \dots, n, \quad (3a)$$

$$\sum_{i=1}^n c_i = C. \quad (3b)$$

Third, the system (2a)–(3b) is completed with the thermodynamic equilibrium:

$$\min_{c_1 > 0, \dots, c_n > 0} \max_{\phi, p} \mathcal{L}(c_1, \dots, c_n, \phi, p, \mu_1, \dots, \mu_n) \quad (4a)$$

for the non-trivial pressure $p(t, x)$ which should be taken into consideration according to the Dreyer generalization, see [19]. The Lagrangian \mathcal{L} in (4a) implies the Landau grand potential

$$\begin{aligned} \mathcal{L}(\mathbf{c}, \phi, p, \boldsymbol{\mu}) = & \int_{\Omega^\varepsilon} \left\{ \sum_{i=1}^n (k_B \theta c_i (\ln(\beta_i c_i) - 1) + z_i c_i \phi) - \frac{1}{2} \nabla \phi^\top A \nabla \phi \right. \\ & \left. + p \left(\frac{1}{C} \sum_{i=1}^n c_i - 1 \right) - \sum_{i=1}^n \mu_i c_i \right\} dx + \int_{\Sigma^\varepsilon} (g\phi - \frac{\alpha}{2} \phi^2) dS_x \end{aligned} \quad (4b)$$

see [26], taken over the pore phase. Here $k_B > 0$ is the Boltzmann constant, and the temperature $\theta > 0$, volume factors of the species $\beta_i > 0$, $i = 1, \dots, n$, the boundary capacitance $\alpha > 0$, and the electric displacement g are assumed to be given. The electric permittivity d -by- d matrix A is assumed symmetric positive definite (spd). Therefore, there exist $0 < \underline{a} \leq \bar{a}$ such that

$$\underline{a}|\nabla\phi|^2 \leq \nabla\phi^\top A \nabla\phi \leq \bar{a}|\nabla\phi|^2 \quad \text{for all } \phi. \quad (4c)$$

From the optimization viewpoint, specie concentrations c_1, \dots, c_n and the electrostatic potential ϕ enter (4b) as the primal variables, while μ_1, \dots, μ_n and p , called the entropy variables, are here dual ones. In fact, electro-chemical potentials and the pressure appear in \mathcal{L} as the Lagrange multipliers, respectively, to the constraints from (3a) and (3b).

The first-order optimality condition for (4a) together with (4b) constitutes three relations:

$$0 = \frac{\partial \mathcal{L}}{\partial p} = \frac{1}{C} \sum_{i=1}^n c_i - 1 \quad (5a)$$

which guarantees the summary volume balance (3b), the identity

$$0 = \frac{\partial \mathcal{L}}{\partial c_i} = k_B \theta \ln(\beta_i c_i) + z_i \phi + \frac{1}{C} p - \mu_i, \quad i = 1, \dots, n \quad (5b)$$

implying the Gibbs–Duhem equation for the electro-chemical potentials, and the Gauss law in the form of the variational equation with a test-function $\bar{\phi}$:

$$0 = \langle \frac{\partial \mathcal{L}}{\partial \phi}, \bar{\phi} \rangle = \int_{\Omega^\varepsilon} \left(\sum_{i=1}^n z_i c_i \bar{\phi} - \nabla \phi^\top A \nabla \bar{\phi} \right) dx + \int_{\Sigma^\varepsilon} (g \bar{\phi} - \alpha \phi \bar{\phi}) dS_x \quad (5c)$$

following the Poisson equation under Robin boundary conditions for the electrostatic potential.

On the basis of the governing equations (2), (5b) and (5c) together with the unilateral constraints in (3), we derive the generalized system of Poisson–Nernst–Planck equations under suitable initial conditions and inhomogeneous, nonlinear boundary conditions at the interface.

4. GENERALIZED POISSON–NERNST–PLANCK MODEL

At the beginning we specify the d -by- d diffusivity matrices D^{11}, \dots, D^{nn} in (2b).

The standard assumption is the ellipticity condition: there exist $0 < \underline{d} \leq \bar{d}$ such that

$$\underline{d} \sum_{k=1}^n |\nabla c_k|^2 \leq \sum_{i,j=1}^n \nabla c_j^\top D^{ij} \nabla c_i \leq \bar{d} \sum_{k=1}^n |\nabla c_k|^2 \quad \text{for all } c_1, \dots, c_n. \quad (6a)$$

For example, if $D^{ij} = d_{ij} \mathbf{I}$, where \mathbf{I} stands for the d -by- d identity matrix, and d_{ij} are scalar numbers, $i, j = 1, \dots, n$, then (6a) holds when the entries d_{ij} constitute a spd-matrix.

For a given, symmetric positive-definite matrix $D = (D_{kl})_{k,l=1}^d$, the key assumption is that

$$\sum_{i=1}^n D^{ij} = D, \quad j = 1, \dots, n, \quad D \in \text{Spd}(\mathbb{R}^{d \times d}). \quad (6b)$$

This definition is closely related to the so-called stochastic matrices. Indeed, recomposing the d -by- d matrix entries $D^{ij} = (D_{kl}^{ij})_{k,l=1}^d$ in the n -by- n matrices $(D_{kl}^{ij})_{i,j=1}^n$ for fixed indexes $k, l \in \{1, \dots, d\}$ the sum in every column $j = 1, \dots, n$ is equal:

$$\sum_{i=1}^n D_{kl}^{ij} = D_{kl} \quad \text{for } j = 1, \dots, n \text{ and fixed } k, l \in \{1, \dots, d\}. \quad (6c)$$

If all entries D_{kl}^{ij} , $i, j = 1, \dots, n$, are non-negative for some index (k, l) , then such matrix in (6c) is called left stochastic when $D_{kl} = 1$, otherwise quasi-stochastic.

A special, particular case of such matrices in (6b) are the "diagonal" and equal diffusivities

$$D^{ij} = D \text{ if } i = j, \text{ and } D^{ij} = 0 \text{ otherwise.} \quad (6d)$$

The assumption (6d) is stronger than (6b), and we will see in Proposition 6 the crucial issue: the weak assumption (6b) guarantees the positivity in (3a) only locally in time, while (6d) globally.

A physical reasoning of (6b) comes necessary from the balance (2c) and (3b) as follows.

From (5b) the quasi-Fermi electro-chemical potentials and its gradients are defined as

$$\mu_i = k_B \theta \ln(\beta_i c_i) + z_i \phi + \frac{1}{C} p, \quad i = 1, \dots, n, \quad (7a)$$

$$\nabla \mu_i = k_B \theta \frac{\nabla c_i}{c_i} + z_i \nabla \phi + \frac{1}{C} \nabla p, \quad i = 1, \dots, n. \quad (7b)$$

Substituting the constitutive equations (2b) together with the expression (7b) in the flux balance equation (2c), using the assumption (6b) after summation over $i = 1, \dots, n$, we have

$$0 = \sum_{i,j=1}^n c_j \nabla \mu_j^\top D^{ij} = \sum_{j=1}^n c_j \nabla \mu_j^\top D = \left\{ k_B \theta \nabla \left(\sum_{j=1}^n c_j \right) + \sum_{j=1}^n z_j c_j \nabla \phi + \frac{1}{C} \left(\sum_{j=1}^n c_j \right) \nabla p \right\}^\top D.$$

Since $\sum_{j=1}^n c_j = C$ in (3b), then $\nabla(\sum_{j=1}^n c_j) = \nabla C = 0$, and we obtain the following identity

$$\nabla p = - \sum_{i=1}^n z_i c_i \nabla \phi. \quad (8)$$

In this respect, it is important to note that (8) appears in [19, 20, 25] as a consequence of the incompressible Navier–Stokes equation for zero barycentric velocity $\mathbf{v} = 0$:

$$\frac{\partial}{\partial t}(\rho \mathbf{v}) + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v}) - \Delta \mathbf{v} + \nabla p = - \sum_{i=1}^n z_i c_i \nabla \phi. \quad (9)$$

The substitution of expression (7b) in the Fickian law (2a) and excluding the pressure p with the help of (8) it results in the strongly nonlinear diffusion equation for the specie concentrations

$$\frac{\partial c_i}{\partial t} = \operatorname{div} \sum_{j=1}^n \left\{ k_B \theta \nabla c_j + c_j \left(z_j - \frac{1}{C} \sum_{k=1}^n z_k c_k \right) \nabla \phi \right\}^\top D^{ij}, \quad i = 1, \dots, n, \quad \text{in } (0, T) \times \Omega^\varepsilon. \quad (10a)$$

The integration by parts of (5c) succeeds in the quasi-linear Poisson equation

$$-\operatorname{div}(\nabla \phi^\top A) - \sum_{i=1}^n z_i c_i = 0 \quad \text{in } (0, T) \times \Omega^\varepsilon \quad (10b)$$

formulated over the pore phase Ω^ε in the time interval $(0, T)$ for arbitrarily fixed $T > 0$.

Proposition 1 (Generalized Poisson–Nernst–Planck model). *The system (10) for c_1, \dots, c_n and ϕ , coupled inherently with the unilateral constraints (3), describes the generalized Poisson–Nernst–Planck model. Determining the entropy variables μ_1, \dots, μ_n and p from relations (7a) and (8), together with conditions (3b) and (6b), the diffusion equation (10a) is equivalent to the governing relations in (2).*

In comparison to (10), the classic Poisson–Nernst–Planck model ignores the pressure and the specie coupling phenomena, when putting $p = 0$ and the diagonal diffusivities $D^{ij} = D^i$ for $j = i$ and zero otherwise, that reduces (10a) to the classic Nernst–Planck law:

$$\frac{\partial}{\partial t} c_i = \operatorname{div}(k_B \theta \nabla c_i + c_i z_i \nabla \phi)^\top D^i, \quad i = 1, \dots, n, \quad D^i \in \mathbb{R}^{d \times d}. \quad (11)$$

The principal drawback is that (11) violates the conservation law of mass (2c).

We endow (10) with initial and boundary conditions. For $\mathbf{c}^{\text{init}} = (c_1^{\text{init}}, \dots, c_n^{\text{init}})^\top$ such that

$$c_i^{\text{init}} > 0, \quad i = 1, \dots, n, \quad (12a)$$

$$\sum_{i=1}^n c_i^{\text{init}} = C \quad (12b)$$

we suppose the usual initial value condition for (10a):

$$c_i(0, \cdot) = c_i^{\text{init}}, \quad i = 1, \dots, n, \quad \text{in } \Omega^\varepsilon \quad \text{as } t = 0. \quad (12c)$$

Given ϕ^D and $\mathbf{c}^D = (c_1^D, \dots, c_n^D)^\top$ in the bath $(0, T) \times \Omega$ such that

$$c_i^D > 0, \quad i = 1, \dots, n, \quad (13a)$$

$$\sum_{i=1}^n c_i^D = C, \quad (13b)$$

and compatible with the initial data

$$c_i^D(0, \cdot) = c_i^{\text{init}}, \quad i = 1, \dots, n, \quad (13c)$$

we set the inhomogeneous Dirichlet condition associated to the bath outer boundary $\partial\Omega$:

$$\phi = \phi^D, \quad c_i = c_i^D, \quad i = 1, \dots, n, \quad \text{on } (0, T) \times \partial\Omega. \quad (13d)$$

Finally, we consider the phase interface Σ^ε between the pores Ω^ε and the solid particles ω^ε , implying here the pore boundary Σ_+^ε and recalling the normal vector ν which is inward to Ω^ε since chosen outward to ω^ε . From the variational equation (5c), using the variational argument, we infer the inhomogeneous Robin boundary condition for the electrostatic potential:

$$-\nabla\phi^\top A\nu + \alpha\phi = g \quad \text{on } (0, T) \times \Sigma^\varepsilon. \quad (14a)$$

A more delicate issue concerns formulation of the inhomogeneous, nonlinear Neumann boundary condition stated for the diffusion fluxes:

$$\sum_{j=1}^n c_j \nabla \mu_j^\top D^{ij} \nu = g_i(c_1, \dots, c_n, \phi), \quad i = 1, \dots, n, \quad \text{on } (0, T) \times \Sigma^\varepsilon \quad (14b)$$

or, plugging the representation (7b) in (14b), it can be expressed equivalently in the entire form

$$\sum_{j=1}^n \left\{ k_B \theta \nabla c_j + c_j \left(z_j - \frac{1}{C} \sum_{k=1}^n z_k c_k \right) \nabla \phi \right\}^\top D^{ij} \nu = g_i(\mathbf{c}, \phi), \quad i = 1, \dots, n \quad (14c)$$

at $(0, T) \times \Sigma^\varepsilon$. The terms $g_i(\mathbf{c}, \phi)$ describe nonlinear boundary reactions at the phase interface. For matching with the constraints (3) it needs proper physical assumptions presented below.

Given nonlinear functions $g_i(\mathbf{c}, \phi)$ have to ensure at $(0, T) \times \Sigma^\varepsilon$: the balance of fluxes

$$\sum_{i=1}^n g_i(\mathbf{c}, \phi) = 0, \quad (14d)$$

the positive production rate, for instance, $g_i(\mathbf{c}, \phi) = c_i^+ \widehat{g}_i$, implying that

$$c_i^- g_i(\mathbf{c}, \phi) = 0, \quad i = 1, \dots, n \quad (14e)$$

where c_i^+ and c_i^- are defined in (15), and a suitable growth condition with $K_{1i}, K_{2i}, K_{3i} \geq 0$:

$$|g_i(\mathbf{c}, \phi)|^2 \leq (K_{1i} + K_{2i} |\phi|^2) G_i(\mathbf{c}), \quad 0 \leq G_i(\mathbf{c}) \leq K_{3i}, \quad i = 1, \dots, n. \quad (14f)$$

We note that just constant boundary fluxes g_i are not admissible in condition (14e).

Next we bring the boundary value problem (10) under initial condition (12c) and boundary conditions (13d), (14a), and (14c) in the form suitable for analysis and present its main results.

5. REDUCED PROBLEM FORMULATION AND ITS ANALYSIS

We exclude the unilateral constraints (3) from the consideration and derive the respectively reduced model without constraints by reformulating the governing equations (10).

With the help of the maximum operator, arbitrary functions c_i (i.e not necessary positive) can be partitioned into distinct the positive c_i^+ and the negative c_i^- parts according to the definition:

$$c_i^+ := \max(0, c_i), \quad c_i^- := \max(0, -c_i) \quad \text{such that } c_i = c_i^+ - c_i^-, \quad c_i^+ c_i^- = 0, \quad i = 1, \dots, n. \quad (15)$$

Using the assumptions (3) on the concentrations and notation (15), we rewrite (10) as

$$\frac{\partial c_i}{\partial t} = \operatorname{div} \sum_{j=1}^n \left\{ k_B \theta \nabla c_j + \frac{C}{\sum_{l=1}^n c_l^+} c_j^+ \left(z_j - \frac{1}{\sum_{l=1}^n c_l^+} \sum_{k=1}^n z_k c_k^+ \right) \nabla \phi \right\}^\top D^{ij}, \quad i = 1, \dots, n, \quad (16a)$$

$$-\operatorname{div}(\nabla \phi^\top A) - \frac{C}{\sum_{l=1}^n c_l^+} \sum_{i=1}^n z_i c_i^+ = 0 \quad \text{in } (0, T) \times \Omega^\varepsilon. \quad (16b)$$

Due to (16a) the Neumann condition (14c) takes the reduced form at $(0, T) \times \Sigma^\varepsilon$:

$$\sum_{j=1}^n \left\{ k_B \theta \nabla c_j + \frac{C}{\sum_{l=1}^n c_l^+} c_j^+ \left(z_j - \frac{1}{\sum_{l=1}^n c_l^+} \sum_{k=1}^n z_k c_k^+ \right) \nabla \phi \right\}^\top D^{ij} \nu = g_i(\mathbf{c}, \phi), \quad i = 1, \dots, n. \quad (17)$$

We formulate the following main results of the analysis of the reduced model.

Proposition 2 (Hierarchy of models). *The reduced model formulation (16) follows from the generalized Poisson–Nernst–Planck equations (10) together with unilateral constraints (3). In return, (10) follows from (16) only if the unilateral constraints (3) hold.*

Indeed, the assertion of Proposition 2 can be checked directly.

Proposition 3 (Well-posedness of the reduced problem). *Under assumptions (4c) and (6a) on the matrices A and D^{11}, \dots, D^{nn} , (13c) on the initial and boundary data, and the growth condition (14f), there exists a weak solution c_1, \dots, c_n and ϕ of the boundary value problem consisting of the reduced equations (16) under the initial condition (12c), the Dirichlet condition (13d), the Robin and nonlinear Neumann boundary conditions (14a) and (17).*

It satisfies the following a-priori estimate: for arbitrarily fixed final time $T > 0$, there exist positive constants $K_\phi, K_c > 0$ depending on the problem data and maybe small $\delta > 0$ such that

$$\sup_{t \in (0, T)} \int_{\Omega^\varepsilon} (\phi^2 + |\nabla \phi|^2) dx \leq K_\phi, \quad (18a)$$

$$\sum_{i=1}^n \left\{ \sup_{t \in (0, T)} \int_{\Omega^\varepsilon} c_i^2 dx + \int_0^T \int_{\Omega^\varepsilon} (c_i^2 + |\nabla c_i|^2) dx dt \right\} \leq \frac{T}{\delta} K_\phi + K_c. \quad (18b)$$

Proof. We sketch the proof, which is based on the technique in [25]. First we ensure the a-priori estimate (18) and then, based on this estimate, we apply the Schauder–Tikhonov fixed-point theorem for a suitable Galerkin approximation.

For arbitrary $\tau \in (0, T)$, multiplying (16a) with smooth test-functions \bar{c}_i , integrating the result by parts over $Q_\tau^\varepsilon := (0, \tau) \times \Omega^\varepsilon$ using the Neumann boundary condition (17) at the

interface Σ^ε , and introducing the notation $S_\tau^\varepsilon := (0, \tau) \times \Sigma^\varepsilon$ for short, we get n variational equations for concentrations for $i = 1, \dots, n$:

$$\begin{aligned} & \int_{Q_\tau^\varepsilon} \left\{ \frac{\partial c_i}{\partial t} \bar{c}_i + \sum_{j=1}^n \left(k_B \theta \nabla c_j + \frac{C c_j^+}{\sum_{l=1}^n c_l^+} \left(z_j - \frac{\sum_{k=1}^n z_k c_k^+}{\sum_{l=1}^n c_l^+} \right) \nabla \phi \right)^\top D^{ij} \nabla \bar{c}_i \right\} dx dt \\ &= \int_{S_\tau^\varepsilon} g_i(c_1, \dots, c_n, \phi) \bar{c}_i dS_x dt \quad \text{for all } \bar{c}_i \text{ such that } \bar{c}_i = 0 \text{ on } (0, T) \times \partial\Omega. \end{aligned} \quad (19a)$$

Multiplying (16b) with a smooth test-function $\bar{\phi}$ and integrating by parts over Ω^ε with the help of the Robin boundary condition (14a) at the interface Σ^ε , we obtain the variational equation for the electrostatic potential (cf. (5c)) in the time interval $t \in (0, T)$:

$$\begin{aligned} & \int_{\Omega^\varepsilon} (\nabla \phi^\top A \nabla \bar{\phi} - \frac{C}{\sum_{l=1}^n c_l^+} \sum_{i=1}^n z_i c_i^+ \bar{\phi}) dx + \int_{\Sigma^\varepsilon} \alpha \phi \bar{\phi} dS_x = \int_{\Sigma^\varepsilon} g \bar{\phi} dS_x \\ & \text{for all test-functions } \bar{\phi} \text{ such that } \bar{\phi} = 0 \text{ on } \partial\Omega. \end{aligned} \quad (19b)$$

The coupled system of nonlinear equations (19) together with the initial condition (12c) and the Dirichlet boundary conditions (13d) implies the weak formulation of the reduced problem.

First we prove (18a). For this task, the test function $\bar{\phi} = \phi - \phi^D =: \hat{\phi}$ for short, which is zero at $\partial\Omega$ due to the first Dirichlet condition in (13d), can be inserted into (19b). This yields

$$\begin{aligned} & \int_{\Omega^\varepsilon} \nabla \hat{\phi}^\top A \nabla \hat{\phi} dx + \int_{\Sigma^\varepsilon} \alpha \hat{\phi}^2 dS_x \\ &= \int_{\Omega^\varepsilon} \left(C \sum_{i=1}^n z_i \frac{c_i^+}{\sum_{l=1}^n c_l^+} \hat{\phi} - \nabla(\phi^D)^\top A \nabla \hat{\phi} \right) dx + \int_{\Sigma^\varepsilon} (g - \alpha \phi^D) \hat{\phi} dS_x. \end{aligned} \quad (20)$$

Using the boundedness $0 \leq \frac{c_i^+}{\sum_{l=1}^n c_l^+} \leq 1$ and the second inequality in (4c), we estimate from above the right-hand side of (20) by Young's inequality with arbitrary weights $\delta_1, \delta_2, \delta_3 > 0$:

$$\begin{aligned} |\nabla(\phi^D)^\top A \nabla \hat{\phi}| &\leq \bar{a}(\delta_1 |\nabla \hat{\phi}|^2 + \frac{1}{4\delta_1} |\nabla \phi^D|^2), \quad \left| \sum_{i=1}^n z_i \frac{c_i^+}{\sum_{l=1}^n c_l^+} \hat{\phi} \right| \leq Z n (\delta_2 \hat{\phi}^2 + \frac{1}{4\delta_2}) \\ |(g - \alpha \phi^D) \hat{\phi}| &\leq (\delta_3 (1 + \alpha) \hat{\phi}^2 + \frac{1}{4\delta_3} (g^2 + \alpha (\phi^D)^2)), \quad Z := \max_{k \in \{1, \dots, n\}} |z_k|. \end{aligned} \quad (21)$$

Further we employ the trace theorem at Σ^ε : there exist constants $0 < \underline{K} \leq \overline{K}$ such that

$$\underline{K} \|u\|_{\Omega^\varepsilon}^2 \leq \int_{\Sigma^\varepsilon} u^2 dx \leq \overline{K} \|u\|_{\Omega^\varepsilon}^2, \quad \|u\|_{\Omega^\varepsilon}^2 := \int_{\Omega^\varepsilon} (u^2 + |\nabla u|^2) dx \quad (22a)$$

and the Poincaré inequality: there exists constant $K_0 > 0$ such that

$$\int_{\Omega^\varepsilon} u^2 dx \leq K_0 \int_{\Omega^\varepsilon} |\nabla u|^2 dx \quad (22b)$$

hold for all smooth, differentiable functions u such that $u = 0$ at $\partial\Omega$.

Estimating the left-hand side of (20) from the first inequality in (4c), applying (21) and (22b) to its right-hand side, and collecting the integral terms, for a constant $\delta_0 > 0$ it follows:

$$\begin{aligned} & ((1 - \delta_0)\underline{a} - \bar{a}\delta_1) \int_{\Omega^\varepsilon} |\nabla \hat{\phi}|^2 dx + (\alpha - (1 + \alpha)\delta_3) \int_{\Sigma^\varepsilon} \hat{\phi}^2 dS_x + \left(\frac{\delta_0 \underline{a}}{K_0} - CnZ\delta_2\right) \\ & \times \int_{\Omega^\varepsilon} \hat{\phi}^2 dx \leq \frac{a}{4\delta_1} \int_{\Omega^\varepsilon} |\nabla \phi^D|^2 dx + \frac{Cn|\Omega^\varepsilon|}{4\delta_2} Z + \frac{1}{4\delta_3} \int_{\Sigma^\varepsilon} (g^2 + \alpha(\phi^D)^2) dS_x =: M_\phi^\delta. \end{aligned} \quad (23)$$

Free parameters $\delta_0, \delta_1, \delta_2, \delta_3$ can be chosen sufficiently small so that all three factors by the integrals in the left-hand side of (23) are positive, hence have a positive lower bound:

$$\min\left\{(1 - \delta_0)\underline{a} - \bar{a}\delta_1, \frac{\delta_0 \underline{a}}{K_0} - CnZ\delta_2, \alpha - (1 + \alpha)\delta_3\right\} =: m_\phi^\delta > 0. \quad (24)$$

Therefore, (23) implies $m_\phi^\delta \|\hat{\phi}\|_{\Omega^\varepsilon}^2 \leq M_\phi^\delta$, where the squared norm is defined in (22a). Decomposing $\|\phi\|_{\Omega^\varepsilon}^2 = \|\phi - \phi^D + \phi^D\|_{\Omega^\varepsilon}^2 \leq 2(\|\hat{\phi}\|_{\Omega^\varepsilon}^2 + \|\phi^D\|_{\Omega^\varepsilon}^2)$, from (23) and (24) for arbitrary time $t \in (0, T)$ we infer the estimate (18a) with the constant $K_\phi = 2\left(\frac{1}{m_\phi^\delta} M_\phi^\delta + \|\phi^D\|_{\Omega^\varepsilon}^2\right)$.

Second we prove (18b). The test functions $\bar{c}_i = c_i - c_i^D =: \hat{c}_i$, $i = 1, \dots, n$, are zero at $(0, T) \times \partial\Omega$ due to the second Dirichlet condition in (13d) and can be inserted into (19a):

$$\begin{aligned} & \int_{Q_\tau^\varepsilon} \left\{ \frac{\partial \hat{c}_i}{\partial t} \hat{c}_i + \sum_{j=1}^n k_B \theta \nabla \hat{c}_j^\top D^{ij} \nabla \hat{c}_i \right\} dx dt = - \int_{Q_\tau^\varepsilon} \left\{ \frac{\partial c_i^D}{\partial t} \hat{c}_i + \sum_{j=1}^n \{ k_B \theta \nabla c_j^D \right. \\ & \left. + \frac{C c_j^+}{\sum_{l=1}^n c_l^+} \left(z_j - \frac{\sum_{k=1}^n z_k c_k^+}{\sum_{l=1}^n c_l^+} \right) \nabla \phi \}^\top D^{ij} \nabla \hat{c}_i \right\} dx dt + \int_{S_\tau^\varepsilon} g_i(\mathbf{c}, \phi) \hat{c}_i dS_x dt, \quad i = 1, \dots, n. \end{aligned} \quad (25)$$

The compatibility (13c) argues the following calculus for the time derivative:

$$\int_{Q_\tau^\varepsilon} \frac{\partial \hat{c}_i}{\partial t} \hat{c}_i dx dt = \frac{1}{2} \int_0^\tau \int_{\Omega^\varepsilon} \frac{\partial \hat{c}_i^2}{\partial t} dx dt = \frac{1}{2} \int_{\Omega^\varepsilon} \hat{c}_i^2 dx \Big|_{t=0}^\tau = \frac{1}{2} \int_{\Omega^\varepsilon} \hat{c}_i^2(\tau, x) dx, \quad i = 1, \dots, n. \quad (26)$$

After summation of (25) over $i = 1, \dots, n$, using the assumption (6a) for D^{11}, \dots, D^{nn} , the boundedness $0 \leq \frac{c_i^+}{\sum_{l=1}^n c_l^+} \leq 1$, the identity (26), and applying Young's inequality we infer

$$\begin{aligned} & \sum_{i=1}^n \left\{ \frac{1}{2} \int_{\Omega^\varepsilon} \hat{c}_i(\tau, x)^2 dx + k_B \theta \bar{d} \int_{Q_\tau^\varepsilon} |\nabla \hat{c}_i|^2 dx dt \right\} \leq \sum_{i=1}^n \left\{ k_B \theta \bar{d} \left(\delta_4 \int_{Q_\tau^\varepsilon} |\nabla \hat{c}_i|^2 dx dt \right. \right. \\ & \left. \left. + \frac{1}{4\delta_4} \int_{Q_\tau^\varepsilon} |\nabla c_i^D|^2 dx dt \right) + ZC(1 + n) \bar{d} \left(\delta_5 \int_{Q_\tau^\varepsilon} |\nabla \hat{c}_i|^2 dx dt + \frac{1}{4\delta_5} \int_{Q_\tau^\varepsilon} |\nabla \phi|^2 dx dt \right) \right. \\ & \left. + \left(\delta_6 \int_{Q_\tau^\varepsilon} \hat{c}_i^2 dx dt + \frac{1}{4\delta_6} \int_{Q_\tau^\varepsilon} \left(\frac{\partial c_i^D}{\partial t} \right)^2 dx dt \right) + \left(\delta_7 \int_{S_\tau^\varepsilon} \hat{c}_i^2 dS_x dt + \frac{1}{4\delta_7} \int_{S_\tau^\varepsilon} g_i^2(\mathbf{c}, \phi) dS_x dt \right) \right\} \end{aligned} \quad (27)$$

with arbitrary weights $\delta_4, \delta_5, \delta_6, \delta_7 > 0$. Collecting the same integral terms in (27), using the growth condition (14f) at the interface S_τ^ε , the trace theorem (22a), and the Poincare inequality (22b), it follows the estimate with arbitrary weights $\delta_8, \delta_9 > 0$:

$$\begin{aligned} & \sum_{i=1}^n \left\{ \frac{1}{2} \int_{\Omega^\varepsilon} \widehat{c}_i(\tau, x)^2 dx + (k_B \theta d(1 - \delta_8 - \delta_9) - k_B \theta \bar{d} \delta_4 - ZC(1+n)\bar{d} \delta_5) \right. \\ & \times \int_{Q_\tau^\varepsilon} |\nabla \widehat{c}_i|^2 dx dt + (k_B \theta d(\frac{\delta_8}{K_0} - \delta_9) - \delta_6) \int_{Q_\tau^\varepsilon} \widehat{c}_i^2 dx dt + (\frac{k_B \theta d}{K} \delta_9 - \delta_7) \int_{S_\tau^\varepsilon} \widehat{c}_i^2 dS_x dt \Big\} \\ & \leq \tau M_\phi^\delta K_\phi + M_c^\delta(\tau) \end{aligned} \quad (28a)$$

where we have used (18a) and the notation:

$$\begin{aligned} M_\phi^\delta &:= \frac{Cn(1+n)\bar{d}}{4\delta_5} Z + \sum_{i=1}^n \frac{K_{2i}K_{3i}}{4\delta_7} |\Sigma^\varepsilon|, \\ M_c^\delta(\tau) &:= \sum_{i=1}^n \left\{ \frac{k_B \theta \bar{d}}{4\delta_4} \int_{Q_\tau^\varepsilon} |\nabla c_i^D|^2 dx dt + \frac{1}{4\delta_6} \int_{Q_\tau^\varepsilon} \left(\frac{\partial c_i^D}{\partial t} \right)^2 dx dt + \frac{K_{1i}K_{3i}}{4\delta_7} |S_\tau^\varepsilon| \right\}. \end{aligned} \quad (28b)$$

Sufficiently small δ_4 – δ_9 guarantee the left-hand side of (28a) to be strongly positive:

$$\begin{aligned} & \min \left\{ \frac{1}{2}, k_B \theta d(1 - \delta_8 - \delta_9) - k_B \theta \bar{d} \delta_4 - ZC(1+n)\bar{d} \delta_5, \right. \\ & \left. k_B \theta d(\frac{\delta_8}{K_0} - \delta_9) - \delta_6, \frac{k_B \theta d}{K} \delta_9 - \delta_7 \right\} =: m_c^\delta > 0. \end{aligned} \quad (28c)$$

Taking the supremum over all $\tau \in (0, T)$ in (28a) and using the decomposition $\|\mathbf{c}\|_{Q_T^\varepsilon}^2 = \|\mathbf{c} - \mathbf{c}^D + \mathbf{c}^D\|_{Q_T^\varepsilon}^2 \leq 2(\|\mathbf{c} - \mathbf{c}^D\|_{Q_T^\varepsilon}^2 + \|\mathbf{c}^D\|_{Q_T^\varepsilon}^2)$ with the squared vector-norm defined by

$$\|\mathbf{c}\|_{Q_T^\varepsilon}^2 := \sum_{i=1}^n \left\{ \sup_{t \in (0, T)} \int_{\Omega^\varepsilon} c_i^2 dx + \int_{Q_T^\varepsilon} (c_i^2 + |\nabla c_i|^2) dx dt \right\} \quad (29)$$

relations (28) lead to the estimate (18b) with $\frac{1}{\delta} = \frac{2}{m_c^\delta} M_\phi^\delta$ and $K_c = 2(\frac{1}{m_c^\delta} M_c^\delta(T) + \|\mathbf{c}^D\|_{Q_T^\varepsilon}^2)$.

Given $\mathbf{c}^{(0)} = (c_1^{(0)}, \dots, c_n^{(0)})^\top$, for $k \in \mathbb{N}_0$ we set the linear approximation of equations (19):

$$\int_{\Omega^\varepsilon} \nabla(\phi^{(k)})^\top A \nabla \bar{\phi} dx + \int_{\Sigma^\varepsilon} \alpha \phi^{(k)} \bar{\phi} = \int_{\Omega^\varepsilon} \frac{C}{\sum_{l=1}^n (c_l^{(k)})^+} \sum_{i=1}^n z_i (c_i^{(k)})^+ \bar{\phi} dx + \int_{\Sigma^\varepsilon} g \bar{\phi} dS_x \quad (30a)$$

for all test-functions $\bar{\phi}$ such that $\bar{\phi} = 0$ on $\partial\Omega$.

$$\begin{aligned} & \int_{Q_\tau^\varepsilon} \left\{ \frac{\partial c_i^{(k+1)}}{\partial t} \bar{c}_i + \sum_{j=1}^n k_B \theta \nabla (c_j^{(k+1)})^\top D^{ij} \nabla \bar{c}_i \right\} dx dt = - \int_{Q_\tau^\varepsilon} \sum_{j=1}^n \frac{C(c_j^{(k)})^+}{\sum_{l=1}^n (c_l^{(k)})^+} (z_j \\ & - \frac{\sum_{l=1}^n z_l (c_l^{(k)})^+}{\sum_{l=1}^n (c_l^{(k)})^+}) \nabla \phi^{(k)} \Big)^\top D^{ij} \nabla \bar{c}_i dx dt + \int_{S_\tau^\varepsilon} g_i(\mathbf{c}^{(k)}, \phi^{(k)}) \bar{c}_i dS_x dt \end{aligned} \quad (30b)$$

for all test-functions \bar{c}_i such that $\bar{c}_i = 0$ on $(0, T) \times \partial\Omega$, $i = 1, \dots, n$

supported by the initial condition (12c) and the Dirichlet boundary conditions (13d).

The mapping of $\mathbf{c}^{(k)} = (c_1^{(k)}, \dots, c_n^{(k)})^\top \mapsto \mathbf{c}^{(k+1)} = (c_1^{(k+1)}, \dots, c_n^{(k+1)})^\top$ defined by (30) is continuous on the ball $\|\mathbf{c}^{(k)}\|_{Q_T^\varepsilon}^2 \leq \frac{T}{\delta} K_\phi + K_c$ due to the estimate (18). Henceforth, there exists an accumulation point of the iterates (30) as $k \rightarrow \infty$ which solves the nonlinear problem (19) under the initial condition (12c) and the Dirichlet conditions (13d). The proof is completed. \square

Proposition 4 (Volume balance). *In addition to Proposition 3, if the weak assumption (6b) on the diffusion matrices D^{11}, \dots, D^{nn} holds, supported by assumptions (12b) on the initial data, (13b) and (14d) on the Dirichlet and Neumann boundary data, then the solution components c_1, \dots, c_n of the reduced problem preserve the summary volume, i.e. satisfy (3b).*

Proof. We plug the combination $\bar{C} := \sum_{i=1}^n c_i - C$, which is zero at $(0, T) \times \partial\Omega$ due to assumption (13b) on the sum of the Dirichlet data, as the test functions $\bar{c}_i = \bar{C}$ in (19a) and sum these equations over $i = 1, \dots, n$. Applying the weak assumption (6b) on the diffusion matrices, assumption (14d) on the sum of the boundary reaction terms, and the identities $\frac{\partial}{\partial t}(\sum_{i=1}^n c_i) = \frac{\partial}{\partial t} \bar{C}$ and $\nabla(\sum_{i=1}^n c_i) = \nabla \bar{C}$ since C is constant, we derive the trivial equality in the right-hand side:

$$\frac{1}{2} \int_{\Omega^\varepsilon} \bar{C}^2(\tau, x) dx + \frac{k_B \theta d}{1+K_0} \int_{Q_T^\varepsilon} (\bar{C}^2 + |\nabla \bar{C}|^2) dx dt \leq \int_{Q_T^\varepsilon} \left\{ \frac{\partial \bar{C}}{\partial t} \bar{C} + k_B \theta \nabla \bar{C}^\top D \nabla \bar{C} \right\} dx dt = 0. \quad (31)$$

To get the lower bound in (31) we have used (22b), the calculus in the manner of (26), supported by assumption (12b) on the sum of the initial data, and $d|\nabla \bar{C}|^2 \leq \nabla \bar{C}^\top D \nabla \bar{C}$. Henceforth, $\bar{C} \equiv 0$ implies that the volume balance (3b) holds in Q_T^ε . The proof is completed. \square

Proposition 5 (Weak maximum principle). *In addition to Proposition 3, if the strong assumption (6d) on the diffusion matrices D^{11}, \dots, D^{nn} holds, supported by assumptions (12a) on the initial data, (13a) and (14e) on the Dirichlet and Neumann boundary data, then the solution components c_1, \dots, c_n of the reduced problem are positive, i.e. satisfy (3a).*

Proof. Employing the partition in positive and negative parts from (15), the negative parts c_i^- are zero at $\partial\Omega$ due to assumption (13a) on the sign of the Dirichlet data, at it can be substituted as the test functions $\bar{c}_i = -c_i^-$ in (19a) for $i = 1, \dots, n$. After summation over $i = 1, \dots, n$, applying the strong assumption (6d) on the diffusion matrices, assumption (14e) on the positive production rate of the interfacial reactions, and the complementarity in (15), we get

$$\int_{Q_T^\varepsilon} \sum_{i=1}^n \left\{ \frac{\partial c_i^-}{\partial t} c_i^- + k_B \theta \nabla (c_i^-)^\top D \nabla c_i^- \right\} dx dt = 0. \quad (32)$$

The calculus in the manner of (26) holds here due to the assumption (12a) on the sign of the initial data. Therefore, taking the supremum over $\tau \in (0, T)$ in (32), in view of $D \in \text{Spd}(\mathbb{R}^{d \times d})$, it results in the estimate $\min\{\frac{1}{2}, \frac{k_B \theta d}{1+K_0}\} \|\mathbf{c}^-\|_{Q_T^\varepsilon}^2 \leq 0$ with the norm defined in (29). This implies $c_i^- \equiv 0$ for $i = 1, \dots, n$ overall in Q_T^ε and the positivity in (3a), thus completing the proof. \square

As a consequence of Propositions 2–5 we infer straightforwardly the existence theorem for the generalized Poisson–Nernst–Planck problem.

Proposition 6 (Well-posedness of the generalized Poisson–Nernst–Planck problem). *Under assumptions made in Propositions 3, 4, and 5 on the diffusion matrices, initial and boundary data, the solution c_1, \dots, c_n and ϕ of the reduced problem solves as well the generalized Poisson–Nernst–Planck equations (16) coupled with the constraints (3) under the initial condition (12c) and the boundary conditions (13d), (14a), and (14c), for arbitrary time intervals $(0, T)$.*

If only the weak assumption (6b) holds instead of the strong one (6d), then there exists a time interval $(0, T)$ with $T > 0$, which may be small, where the solution components c_1, \dots, c_n of the reduced problem remain still positive by continuity, hence c_1, \dots, c_n and ϕ solve the generalized Poisson–Nernst–Planck problem locally in this time $(0, T)$.

Moreover, if a solution component ϕ is smooth such that its gradient $\nabla\phi$ is bounded uniformly in the supremum-norm, and the boundary reaction terms $g_1(\mathbf{c}, \phi), \dots, g_n(\mathbf{c}, \phi)$ are sufficiently small, then the solution c_1, \dots, c_n and ϕ is unique.

Proof. For uniqueness of the solution, we sketch the proof based on the technique from [27].

Let $\mathbf{c}^{(1)} = (c_1^{(1)}, \dots, c_n^{(1)})$, $\phi^{(1)}$ and $\mathbf{c}^{(2)} = (c_1^{(2)}, \dots, c_n^{(2)})$, $\phi^{(2)}$ be two distinctive, weak solutions of the generalized Poisson–Nernst–Planck problem, that is (cf. (19)) for $k = 1, 2$:

$$\begin{aligned} & \int_{Q_\tau^\varepsilon} \left\{ \frac{\partial c_i^{(k)}}{\partial t} \bar{c}_i + \sum_{j=1}^n \left(k_B \theta \nabla c_j^{(k)} + c_j^{(k)} \left(z_j - \frac{1}{C} \sum_{l=1}^n z_l c_l^{(k)} \right) \nabla \phi^{(k)} \right)^\top D^{ij} \nabla \bar{c}_i \right\} dx dt \\ &= \int_{S_\tau^\varepsilon} g_i(\mathbf{c}^{(k)}, \phi^{(k)}) \bar{c}_i dS_x dt \quad \text{for all } \bar{c}_i \text{ such that } \bar{c}_i = 0 \text{ on } (0, T) \times \partial\Omega, \quad i = 1, \dots, n, \end{aligned} \quad (33a)$$

$$\int_{\Omega^\varepsilon} \left(\nabla(\phi^{(k)})^\top A \nabla \bar{\phi} - \sum_{i=1}^n z_i c_i^{(k)} \bar{\phi} \right) dx + \int_{\Sigma^\varepsilon} \alpha \phi^{(k)} \bar{\phi} dS_x = \int_{\Sigma^\varepsilon} g \bar{\phi} dS_x \quad (33b)$$

for all test-functions $\bar{\phi}$ such that $\bar{\phi} = 0$ on $\partial\Omega$

coupled with the constraints (3) under the initial (12c) and the Dirichlet (13d) conditions.

Its difference denoted by $(\tilde{c}_1, \dots, \tilde{c}_n)^\top = \tilde{\mathbf{c}} := \mathbf{c}^{(1)} - \mathbf{c}^{(2)}$ and $\tilde{\phi} := \phi^{(1)} - \phi^{(2)}$ satisfies

$$\begin{aligned} & \int_{\Omega^\varepsilon} \left\{ \frac{\partial \tilde{c}_i}{\partial t} \tilde{c}_i + \sum_{j=1}^n k_B \theta \nabla \tilde{c}_j^\top D^{ij} \nabla \tilde{c}_i \right\} dx = \int_{\Sigma^\varepsilon} (g_i(\mathbf{c}^{(1)}, \phi^{(1)}) - g_i(\mathbf{c}^{(2)}, \phi^{(2)})) \tilde{c}_i dS_x \\ & - \int_{\Omega^\varepsilon} \left(c_j^{(1)} \left(z_j - \sum_{l=1}^n z_l \frac{c_l^{(1)}}{C} \right) \nabla \phi^{(1)} - c_j^{(2)} \left(z_j - \sum_{l=1}^n z_l \frac{c_l^{(2)}}{C} \right) \nabla \phi^{(2)} \right)^\top D^{ij} \nabla \tilde{c}_i dx, \end{aligned} \quad (34a)$$

$$\int_{\Omega^\varepsilon} \nabla \tilde{\phi}^\top A \nabla \tilde{\phi} dx + \int_{\Sigma^\varepsilon} \alpha \tilde{\phi}^2 dS_x = \int_{\Omega^\varepsilon} \sum_{i=1}^n z_i \tilde{c}_i \tilde{\phi} dx, \quad (34b)$$

$$\tilde{\phi} = \tilde{c}_1 = \dots = \tilde{c}_n = \sum_{i=1}^n \tilde{c}_i = 0 \text{ on } \{0\} \times \Omega^\varepsilon \text{ and } (0, T) \times \partial\Omega. \quad (34c)$$

The relations (34) hold for arbitrary $t \in (0, T)$, they are derived from (33) by skipping the time-integration in (33a) and the subsequent substitution of the test-functions $\bar{c}_i = \tilde{c}_i$, $i = 1, \dots, n$, and $\bar{\phi} = \tilde{\phi}$ which are zero at $(0, T) \times \partial\Omega$. We assume that there exists

$$\max_{k \in \{1, 2\}} \left\{ \sup_{(t, x) \in Q_T^\varepsilon} (|\phi^{(k)}| + |\nabla \phi^{(k)}|) \right\} =: M_\phi^T < \infty \quad (35a)$$

and the boundary reaction terms are such that its disturbance can be estimated (cf. (14f)) as

$$\left| \sum_{i=1}^n (g_i(\mathbf{c}^{(1)}, \phi^{(1)}) - g_i(\mathbf{c}^{(2)}, \phi^{(2)})) \tilde{c}_i \right| \leq \tilde{G}(\mathbf{c}^{(1)}, \phi^{(1)}, \mathbf{c}^{(2)}, \phi^{(2)}) \sum_{i=1}^n \tilde{c}_i^2, \quad (35b)$$

where $0 \leq \tilde{G}(\mathbf{c}^{(1)}, \phi^{(1)}, \mathbf{c}^{(2)}, \phi^{(2)}) \leq \delta_{10} < \frac{k_B \theta d}{K}$ and δ_{10} maybe small.

Applying Young's inequality to (34b) with the weight $\delta_{11} = \frac{\alpha K}{Z}$ and using (4c) and (22a) due to the homogeneous Dirichlet condition at $\partial\Omega$, we estimate straightforwardly

$$\int_{\Omega^\varepsilon} |\nabla \tilde{\phi}|^2 dx \leq \tilde{K}_\phi \int_{\Omega^\varepsilon} \sum_{i=1}^n \tilde{c}_i^2 dx, \quad \tilde{K}_\phi = \frac{Z^2}{4\alpha K(a + \alpha K)}, \quad Z := \max_{k \in \{1, \dots, n\}} |z_k|. \quad (36)$$

With the help of (34c), (35), and (36), applying Young's inequality to (34a) such that

$$\begin{aligned} & \sum_{i,j=1}^n \left\{ c_j^{(1)} \left(z_j - \sum_{l=1}^n z_l \frac{c_l^{(1)}}{C} \right) \nabla \phi^{(1)} - c_j^{(2)} \left(z_j - \sum_{l=1}^n z_l \frac{c_l^{(2)}}{C} \right) \nabla \phi^{(2)} \right\}^\top D^{ij} \nabla \tilde{c}_i \\ &= \sum_{i,j=1}^n \left\{ \tilde{c}_j \left(z_j - \sum_{l=1}^n z_l \frac{c_l^{(1)}}{C} \right) \nabla \phi^{(1)} + c_j^{(2)} \left(z_j - \sum_{l=1}^n z_l \frac{c_l^{(2)}}{C} \right) \nabla \tilde{\phi} - \frac{c_j^{(2)}}{C} \sum_{l=1}^n z_l \tilde{c}_l \nabla \phi^{(1)} \right\}^\top D^{ij} \nabla \tilde{c}_i \\ &\leq Z \bar{d} \sum_{i=1}^n \left\{ (1+n) M_\phi^T (\delta_{12} |\nabla \tilde{c}_i|^2 + \frac{1}{4\delta_{12}} \tilde{c}_i^2) + (1+n) C (\delta_{13} |\nabla \tilde{c}_i|^2 + \frac{\tilde{K}_\phi}{4\delta_{13}} \sum_{l=1}^n \tilde{c}_l^2) \right. \\ &\quad \left. + M_\phi^T (\delta_{14} |\nabla \tilde{c}_i|^2 + \frac{\tilde{K}_\phi}{4\delta_{14}} (\sum_{l=1}^n \tilde{c}_l)^2) \right\} \end{aligned}$$

similarly to the lines in the proof of Proposition 3 we estimate for $t \in (0, T)$:

$$\begin{aligned} & \tilde{k}_c \int_{\Omega^\varepsilon} \sum_{i=1}^n |\nabla \tilde{c}_i|^2 dx + \frac{1}{2} \frac{d}{dt} \int_{\Omega^\varepsilon} \sum_{i=1}^n \tilde{c}_i^2 dx \leq \tilde{K}_c \int_{\Omega^\varepsilon} \sum_{i=1}^n \tilde{c}_i^2 dx, \\ & \text{where } \tilde{K}_c := \delta_{10} \bar{K} + Z \bar{d} \left(\frac{(1+n) M_\phi^T}{4\delta_{12}} + \frac{n(1+n) C \tilde{K}_\phi}{4\delta_{13}} + \frac{n^2 M_\phi^T \tilde{K}_\phi}{4\delta_{14}} \right), \\ & \tilde{k}_c := k_B \theta d - \delta_{10} \bar{K} - Z \bar{d} ((1+n) M_\phi^T \delta_{12} + (1+n) C \delta_{13} + M_\phi^T \delta_{14}). \end{aligned} \quad (37)$$

Choosing the parameters $\delta_{12}, \delta_{13}, \delta_{14}$ sufficiently small so that $\tilde{k}_c \geq 0$, we integrate the inequality (37) and obtain due to the initial condition in (34c) that

$$0 \leq \int_{\Omega^\varepsilon} \sum_{i=1}^n \tilde{c}_i^2(t, x) dx \leq e^{2\tilde{K}_c t} \int_{\Omega^\varepsilon} \sum_{i=1}^n \tilde{c}_i^2(0, x) dx = 0. \quad (38)$$

Hence $\tilde{c} \equiv 0$ in Q_T^ε and $\tilde{\phi} \equiv 0$ due to (36) that proves the uniqueness under assumption (35). \square

Proposition 7 (Entropy estimate and stability). *Let the Dirichlet data c_i^D be constant, $\beta_i = \frac{1}{c_i^D}$, satisfy the charge-neutrality condition $\sum_{i=1}^n z_i c_i^D = 0$, and the coefficient matrices be scalar $A = \underline{a}I$ and $D^{ij} = \underline{d}\delta_{ij}I$ with the Kronecker-delta δ_{ij} , $i, j = 1, \dots, n$. For a non-negative entropy defined for the solution of generalized Poisson–Nernst–Planck problem as*

$$S := k_B C |\Omega^\varepsilon| - \frac{\partial \mathcal{L}}{\partial \theta} = k_B \int_{\Omega^\varepsilon} \left\{ C - \sum_{i=1}^n c_i \left(\ln\left(\frac{c_i}{c_i^D}\right) - 1 \right) \right\} dx = -k_B \int_{\Omega^\varepsilon} \sum_{i=1}^n c_i \ln\left(\frac{c_i}{c_i^D}\right) dx, \quad (39)$$

the entropy dissipation characterizing the system stability has then the following expression:

$$\begin{aligned} \frac{dS}{dt} = & k_B \underline{d} \int_{\Omega^\varepsilon} \left\{ k_B \theta \sum_{i=1}^n 4 |\nabla(\sqrt{c_i})|^2 + \frac{1}{\underline{a}} \left(\sum_{i=1}^n z_i c_i \right)^2 \right\} dx \\ & - k_B \int_{\Sigma^\varepsilon} \left\{ \sum_{i=1}^n g_i(\mathbf{c}, \phi) \ln\left(\frac{c_i}{c_i^D}\right) + \frac{\underline{d}}{\underline{a}} (\alpha \phi - g) \left(\sum_{i=1}^n z_i c_i \right) \right\} dS_x. \end{aligned} \quad (40)$$

The entropy inequality $\frac{dS}{dt} \geq 0$ can be ensured for small boundary terms $g_i(\mathbf{c}, \phi)$ and $\alpha \phi - g$.

Proof. We consider the weak solution c_1, \dots, c_n and ϕ of the generalized Poisson–Nernst–Planck problem satisfying the variational equations in (33) (without the super-index (k)).

Then $S \geq 0$ in (39) is provided by $\frac{c_i}{c_i^D} \ln\left(\frac{c_i}{c_i^D}\right) \geq \frac{c_i}{c_i^D} - 1$ and the volume balance (3b) and (13b). Following [28], we substitute the test functions $\bar{c}_i = \ln\left(\frac{c_i}{c_i^D}\right)$ in (33a) since $\ln\left(\frac{c_i}{c_i^D}\right) = \ln 1 = 0$ at $\partial\Omega$, skipping the time integration, and $\bar{\phi} = \sum_{l=1}^n z_l c_l$ in (33b), due to the charge-neutrality condition. Using the assumption on the coefficient matrices and $\nabla\left(\ln\left(\frac{c_i}{c_i^D}\right)\right) = \frac{\nabla c_i}{c_i}$ it implies:

$$\begin{aligned} & \int_{\Omega^\varepsilon} \left\{ \frac{\partial c_i}{\partial t} \ln\left(\frac{c_i}{c_i^D}\right) + \underline{d} \left\{ k_B \theta \nabla c_i + c_i \left(z_i - \frac{1}{C} \sum_{l=1}^n z_l c_l \right) \nabla \phi \right\}^\top \frac{\nabla c_i}{c_i} \right\} dx \\ & = \int_{\Sigma^\varepsilon} g_i(\mathbf{c}, \phi) \ln\left(\frac{c_i}{c_i^D}\right) dS_x, \quad i = 1, \dots, n, \end{aligned} \quad (41a)$$

$$\int_{\Omega^\varepsilon} \left\{ \underline{a} \nabla \phi^\top \nabla \left(\sum_{l=1}^n z_l c_l \right) - \left(\sum_{l=1}^n z_l c_l \right)^2 \right\} dx = \int_{\Sigma^\varepsilon} (g - \alpha \phi) \left(\sum_{l=1}^n z_l c_l \right) dS_x. \quad (41b)$$

We sum (41a) over $i = 1, \dots, n$, multiplied with k_B , and subtract (41b) multiplied with the factor $\frac{k_B \underline{d}}{\underline{a}}$. Due to $\int_{\Omega^\varepsilon} \sum_{l=1}^n \frac{\partial c_l}{\partial t} \ln\left(\frac{c_l}{c_l^D}\right) = -\frac{1}{k_B} \frac{dS}{dt}$ according to (39) and $\frac{\partial}{\partial t} \left(\sum_{l=1}^n c_l \right) = 0$, using the identities $\nabla \left(\sum_{l=1}^n c_l \right) = 0$ and $\frac{|\nabla c_i|^2}{c_i} = 4 |\nabla(\sqrt{c_i})|^2$ since $c_i > 0$ in (41a), this yields (40), hence proves the assertion. \square

6. STATIONARY STATE AND HOMOGENIZATION

For homogenization as $\varepsilon \searrow 0^+$ we rely on the static model and extend it in the solid phase underlying the pure diffusion process, see the background in [1]. The domain Ω is partitioned by indicator functions such that $\mathbf{1}_{\Omega^\varepsilon} = 1$, $\mathbf{1}_{\omega^\varepsilon} = 0$ in the pore space $\Omega^\varepsilon \cup \Sigma_+^\varepsilon$ and $\mathbf{1}_{\Omega^\varepsilon} = 0$, $\mathbf{1}_{\omega^\varepsilon} = 1$ in the solid particles $\omega^\varepsilon \cup \Sigma_-^\varepsilon$. The governing equations (10) and (7a) turn into, respectively:

$$-\operatorname{div} \sum_{j=1}^n c_j \nabla \mu_j^\top D_\varepsilon^{ij} = 0, \quad i = 1, \dots, n, \quad -\operatorname{div}(\nabla \phi^\top A_\varepsilon) = \mathbf{1}_{\Omega^\varepsilon} \sum_{i=1}^n z_i c_i, \quad (42a)$$

$$\mu_i = k_B \theta \ln(\beta_i c_i) + \mathbf{1}_{\Omega^\varepsilon} z_i \phi + \frac{1}{C} p, \quad i = 1, \dots, n, \quad \text{in } \Omega^\varepsilon \cup \omega^\varepsilon \quad (42b)$$

with periodically oscillating coefficient matrices $D_\varepsilon^{ij} := D^{ij}(\frac{x}{\varepsilon})$, $A_\varepsilon := A(\frac{x}{\varepsilon})$, see e.g. [16], and supported by the transmission conditions depending on the homogenization parameter ε :

$$-\sum_{j=1}^n c_j \nabla \mu_j^\top D_\varepsilon^{ij} \nu = \varepsilon g_i(\mathbf{c}, \phi) \mathbf{1}_{\Omega^\varepsilon}, \quad -\nabla \phi^\top A_\varepsilon \nu + \frac{\alpha}{\varepsilon} \llbracket \phi \rrbracket = -\varepsilon g \mathbf{1}_{\omega^\varepsilon} \quad \text{on } \Sigma_\pm^\varepsilon \quad (42c)$$

for $i = 1, \dots, n$, with the notation $\llbracket \phi \rrbracket := \phi|_{\Sigma_+^\varepsilon} - \phi|_{\Sigma_-^\varepsilon}$ of the jump across Σ^ε . The jump is taken positive from Ω^ε to ω^ε corresponding to the normal vector ν pointing away from the domain ω^ε .

Together with the Dirichlet condition (13d), the problem (42a) and (42c) after multiplication with proper test-functions and integration by parts over $\Omega^\varepsilon \cup \omega^\varepsilon$ yields the following weak form:

$$\int_{\Omega^\varepsilon \cup \omega^\varepsilon} \sum_{j=1}^n c_j \nabla \mu_j^\top D_\varepsilon^{ij} \nabla \bar{c}_i dx = \int_{\Sigma_+^\varepsilon} \varepsilon g_i(\mathbf{c}, \phi) \bar{c}_i dS_x, \quad i = 1, \dots, n, \quad (43a)$$

for all test-functions \bar{c}_i in $\Omega^\varepsilon \cup \omega^\varepsilon$ allowing jump across Σ^ε and $\bar{c}_i = 0$ on $\partial\Omega$,

$$\int_{\Omega^\varepsilon \cup \omega^\varepsilon} (\nabla \phi^\top A_\varepsilon \nabla \bar{\phi} - \mathbf{1}_{\Omega^\varepsilon} \sum_{i=1}^n z_i c_i \bar{\phi}) dx + \int_{\Sigma^\varepsilon} \frac{\alpha}{\varepsilon} \llbracket \phi \rrbracket \llbracket \bar{\phi} \rrbracket dS_x = \int_{\Sigma_-^\varepsilon} \varepsilon g \bar{\phi} dS_x \quad (43b)$$

for all test-functions $\bar{\phi}$ in $\Omega^\varepsilon \cup \omega^\varepsilon$ allowing jump across Σ^ε and $\bar{\phi} = 0$ on $\partial\Omega$.

Excluding p from (42b) due to (3b) we arrive at the quasi-Fermi statistics, for $i = 1, \dots, n$:

$$c_i = \frac{C \frac{1}{\beta_i} \exp\left(\frac{1}{k_B \theta} (\mu_i - \mathbf{1}_{\Omega^\varepsilon} z_i \phi)\right)}{\sum_{l=1}^n \frac{1}{\beta_l} \exp\left(\frac{1}{k_B \theta} (\mu_l - \mathbf{1}_{\Omega^\varepsilon} z_l \phi)\right)}, \quad p = k_B \theta C \ln \left[\frac{C}{\sum_{l=1}^n \frac{1}{\beta_l} \exp\left(\frac{1}{k_B \theta} (\mu_l - \mathbf{1}_{\Omega^\varepsilon} z_l \phi)\right)} \right] \quad (43c)$$

where the concentrations fulfill naturally the positivity and the volume balance in (3), and the pressure p is a redundant variable. We note that for zero fluxes $g_i(\mathbf{c}, \phi)$ avoiding boundary reactions and $\mu_i = 0$ in (43a), that reduces (43c) to the Boltzmann statistics, see [2].

Following [7], the formal homogenization of (43) yields the following result.

Proposition 8 (Averaged static model). *Under the periodicity assumption, given the surface area $\varkappa_S := \frac{|\partial\omega|}{|Y|}$ and volume $\varkappa_V := \frac{|Y^P|}{|Y|}$ fractions of porosity, $Y^P := Y \setminus \overline{\omega}$, for g and g_i defined in Ω , the averaged homogeneous model corresponding to the heterogeneous model (43) reads:*

$$\int_{\Omega} \sum_{j=1}^n c_j \nabla \mu_j^{\top} D_{\text{eff}}^{ij} \nabla \bar{c}_i dx = \varkappa_S \int_{\Omega} g_i(\mathbf{c}, \phi) \bar{c}_i dx, \quad i = 1, \dots, n, \quad (44a)$$

for all test-functions \bar{c}_i such that $\bar{c}_i = 0$ on $\partial\Omega$,

$$\int_{\Omega} (\nabla \phi^{\top} A_{\text{eff}} \nabla \bar{\phi} - \varkappa_V \sum_{i=1}^n z_i c_i \bar{\phi}) dx = \varkappa_S \int_{\Omega} g \bar{\phi} dx \quad \text{for all } \bar{\phi} \text{ such that } \bar{\phi} = 0 \text{ on } \partial\Omega, \quad (44b)$$

$$c_i = \frac{C \frac{1}{\beta_i} \exp\left(\frac{1}{k_B \theta} (\mu_i - \varkappa_V z_i \phi)\right)}{\sum_{l=1}^n \frac{1}{\beta_l} \exp\left(\frac{1}{k_B \theta} (\mu_l - \varkappa_V z_l \phi)\right)}, \quad i = 1, \dots, n \quad (44c)$$

where the effective coefficient d -by- d matrices in a cell Y containing a solid particle $\omega \subset Y$:

$$D_{\text{eff}}^{ij} = \frac{1}{|\Upsilon|} \int_{Y^P \cup \omega} \left(\frac{\partial}{\partial x} M + I \right) D^{ij} dy, \quad A_{\text{eff}} = \frac{1}{|\Upsilon|} \int_{Y^P \cup \omega} \left(\frac{\partial}{\partial x} \Phi + I \right) A dy \quad (44d)$$

are found from the cell problems: Find vectors M, Φ with the zero average such that

$$\begin{aligned} \int_{Y^P \cup \omega} \left(\frac{\partial}{\partial x} M + I \right) D^{ij} \nabla u dy + \int_{\partial\omega} \alpha \llbracket M \rrbracket \llbracket u \rrbracket dS_y &= 0, \quad i, j = 1, \dots, n, \\ \int_{Y^P \cup \omega} \left(\frac{\partial}{\partial x} \Phi + I \right) A \nabla u dy + \int_{\partial\omega} \alpha \llbracket \Phi \rrbracket \llbracket u \rrbracket dS_y &= 0 \quad \text{for all periodic test-functions } u. \end{aligned} \quad (44e)$$

7. CONCLUSION

A generalized Poisson–Nernst–Planck system on a multi-phase medium preserving the mass conservation is modeled within the Gibbs simplex. The generalized model takes nonlinear reaction terms at the pore-particle phase interface into the consideration.

In the variational framework, the positivity and the volume balance constraints associate the respective entropy variables. The rigorous analysis of the problem is supported by a-priori estimates providing the well-posedness, stability, and homogenization of the stationary state.

For numerical techniques adopted for solution of the non-linear Poisson–Nernst–Planck equations, see [20]. Also we refer to e.g. [29, 30] for advanced, generalized Newton-type, numerical methods in the context of non-linear optimization subject to unilateral constraints.

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