The generalized Poisson–Nernst–Planck system with nonlinear interface conditions

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1 Overwiew

Our modeling deals with the following topics:

- Discontinuous solution in a two-phase medium
- Nonlinear reactions at the phase interface
- Taking pressure into account (as a consequence of the Navier–Stokes equations)
- Volume balance and positivity of concentrations

It leads well-posedness analysis with respect to the following issues:

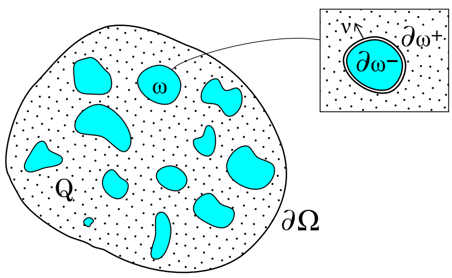
- Generalized formulation coupled with dual entropy variables and constraints
- Existence theorem based on the reduced formulation without constraints
- A priori energy and entropy estimates
- Weak maximum principle
- Uniqueness in a special case
- Lyapunov stability

This system is motivated by applications to modeling of electro–kinetic phenomena in bio- and electro–chemistry. Our specific interest concerns modeling of lithium ion batteries.

2 Formulation of the problem

2.1 Geometry

The two-phase domain $\Omega = Q \cup \omega \cup \partial\omega$ in $\mathbb{R}^d$ consists of two disjoint parts, which are Q pore phase and ω solid phase with the interface $\partial\omega$. We introduce the notation of a jump over the interface: $[\![\cdot]\!] = \cdot|_{\partial\omega^+} - \cdot|_{\partial\omega^-}$.



Research Perspectives CRM Barcelona, Summer 2016, vol. 10, in Trends in Mathematics
Springer-Birkhäuser, Basel

2.2 The generalized Poisson–Nernst–Planck system

For charge species $i = 1, \dots, n$ in $(0,T) \times (Q \cup \omega)$ we state the following governing equations:

(1a) the Fick's law of diffusion: $$\frac{\partial c_i}{\partial t} - \mathrm{div} J_i = 0$$

(1b) with diffusion fluxes: $$J_i = \sum_{j=1}^{n} c_j (\nabla \mu_j)^\top m_i D^{ij};$$

quasi–Fermi electro-chemical potentials:

(1c) $$\mu_i = k_B \Theta \ln(\beta_i c_i) + \mathbf{1}_Q \frac{1}{N_A} \Big(\frac{1}{C} p + z_i \varphi \Big);$$

(1d) the force balance in pore Q : $$\nabla p = - \Big(\sum_{k=1}^{n} z_k c_k \Big) \nabla \varphi;$$

(1e) the Gauss's flux law: $$- \mathrm{div}((\nabla \varphi)^\top A) = \mathbf{1}_Q \sum_{k=1}^{n} z_k c_k.$$

Here the following notations were used: c_i are concentrations of charged species with the charge numbers z_i, respectively, and the summary concentration C, J_i are diffusion fluxes, D^{ij} are diffusivity matrices in $\mathbb{R}^{d \times d}$, φ is the electrostatic potential, μ_i are quasi–Fermi (electrochemical) potentials, A is the electric permittivity, spd–matrix in $\mathbb{R}^{d \times d}$, p is pressure, g_i are boundary fluxes of species, g is the electric flux through boundary, $\mathbf{1}_Q$ is the indicator function of the domain Q, $i, j = 1, \dots, n$.

The system (1) is supplemented by the following boundary and initial conditions.

(2) Dirichlet conditions: $$c_i = c_i^D, \quad i = 1, \dots, n, \quad \text{and} \quad \varphi = \varphi^D \quad \text{on } (0,T) \times \partial\Omega.$$

Interface conditions:

(3a) $$[\![J_i]\!] \nu = 0, \quad -J_i \nu = g_i(\hat{\mathbf{c}}, \hat{\varphi}) \quad \text{on } (0,T) \times \partial\omega;$$

(3b) $$[\![(\nabla\varphi)^\top A]\!] \nu = 0, \quad -(\nabla\varphi)^\top A \nu + \alpha [\![\varphi]\!] = g \quad \text{on } (0,T) \times \partial\omega,$$

where $g_i(\hat{\mathbf{c}}, \hat{\varphi})$ can depend nonlinearly on $(\hat{\mathbf{c}}, \hat{\varphi}) = (\mathbf{c}|_{\partial\omega^+}, \mathbf{c}|_{\partial\omega^-}, \varphi|_{\partial\omega^+}, \varphi|_{\partial\omega^-})$.

(4) Initial conditions: $$c_i = c_i^{in} \quad \text{on } Q \cup \omega.$$

For physical consistency, field variables should satisfy the thermodynamic properties:

(5a) Positivity of concentrations: $$c_i > 0, \quad i = 1, \dots, n, \quad \text{in } (0,T) \times (Q \cup \omega);$$

(5b) Volume balance: $$\sum_{i=1}^{n} c_i = C \quad \text{in } (0,T) \times (Q \cup \omega);$$

(5c) Flux balance: $$\sum_{i=1}^{n} J_i = 0 \quad \text{in} \quad (0,T) \times (Q \cup \omega).$$

The property (5c) follows from volume balance (5b) and diffusivity property (9). The initial data $\mathbf{c}^{in}$ and the boundary data $\mathbf{c}^D$ satisfy positivity and the volume balance in the manner of (5a) and (5b) as well as the compatibility condition $c_i^D(0, \cdot) = c_i^{in}$ in $Q \cup \omega$ for $i = 1, \dots, n$.

2.3 Assumptions

Nonlinear boundary data satisfy the following assumptions:

Growth conditions with $\gamma_1^i \geqslant 0$ and $\gamma_2^i \geqslant 0$ for $i = 1, \dots, n$:

$$\int_{\partial\omega} |g_i(\hat{\mathbf{c}}, \hat{\varphi})|^2 \, dS_x \leqslant \gamma_1^i + \gamma_2^i ||\varphi||^2_{L^2(0,T;H^1(Q)\times H^1(\omega))}; \tag{6}$$

$$\text{Mass balance:} \quad \sum_{i=1}^{n} g_i(\hat{\mathbf{c}}, \hat{\varphi}) = 0 \quad \text{on} \quad (0,T) \times \partial\omega; \tag{7}$$

$$\text{Positive production rate:} \quad g_i(\hat{\mathbf{c}}, \hat{\varphi})[\![c_i^-]\!] = 0 \quad \text{on } (0,T) \times \partial\omega,\ i = 1, \dots, n, \tag{8}$$

where $c_i^+ := \max\{0, c_i\}$, $c_i^- := -\min\{0, c_i\}$ for $i = 1, \dots, n$.

We assume that the coefficient matrices A, $m_i D^{ij}$, and D are symmetric and positive definite (spd). The diffusivity matrices $m_i D^{ij}$ satisfy

$$\text{either the weak assumption:} \qquad \sum_{i=1}^{n} m_i D^{ij} = D, \quad j = 1, \dots, n; \tag{9}$$

$$\text{or the strong assumption:} \qquad m_i D^{ij} = \delta_{ij} D, \quad i, j = 1, \dots, n. \tag{10}$$

2.4 Weak formulation of the problem

Find discontinuous functions $c_1, \dots, c_n$, and φ such that $c_i \in L^\infty(0,T; L^2(Q) \times L^2(\omega)) \cap L^2(0,T; H^1(Q) \times H^1(\omega))$, $\varphi \in L^\infty(0,T; H^1(Q) \times H^1(\omega))$, $c_i \nabla \varphi_i \in L^2((0,T) \times (Q \cup \omega))$ for $i = 1, \dots, n$, which satisfy the Dirichlet boundary conditions, the initial conditions, the volume balance and positivity, as well as fulfill the following variational equations:

$$\int_0^T\!\!\int_{Q\cup\omega} \Big\{ \frac{\partial c_i}{\partial t} \bar{c}_i + \sum_{j=1}^{n} \Big[k_B \Theta \nabla c_j + \mathbf{1}_Q \Upsilon_j(\mathbf{c}) \nabla \varphi \Big]^\top m_i D^{ij} \nabla \bar{c}_i \Big\} \, dx \, dt = \int_0^T\!\!\int_{\partial\omega} g_i(\hat{\mathbf{c}}, \hat{\varphi}) [\![\bar{c}_i]\!] \, dS_x \, dt, \tag{11a}$$

$$\int_{Q\cup\omega} (\nabla\varphi^\top A \nabla\bar{\varphi} - \mathbf{1}_Q \Upsilon(\mathbf{c}) \bar{\varphi}) \, dx + \int_{\partial\omega} \alpha [\![\varphi]\!][\![\bar{\varphi}]\!] \, dS_x = \int_{\partial\omega} g [\![\bar{\varphi}]\!] \, dS_x, \tag{11b}$$

for all test functions $\bar{c}_i \in H^1(0,T; L^2(Q) \times L^2(\omega)) \cap L^2(0,T; H^1(Q) \times H^1(\omega))$ and $\bar{\varphi} \in H^1(Q) \times H^1(\omega)$ such that $\bar{c}_i = 0$ on $(0,T) \times \partial\Omega$ and $\bar{\varphi} = 0$ on $\partial\Omega$, where $\Upsilon_j(\mathbf{c}) := \frac{1}{N_A} c_j \Big(z_j - \frac{1}{C} \Upsilon(\mathbf{c}) \Big)$ and $\Upsilon(\mathbf{c}) := \sum_{k=1}^n z_k c_k$.

3 Well-posedness analysis

The reduced formulation appears after excluding μ_i and p and reducing the constraints (5a)–(5b), where nonlinear terms $\Upsilon(\mathbf{c})$ and $\Upsilon_j(\mathbf{c})$ are replaced by $\Gamma(\mathbf{c}^+) := C \frac{\sum_{k=1}^n z_k c_k^+}{\sum_{k=1}^n c_k^+}$ and $\Gamma_j(\mathbf{c}^+) := \frac{C}{N_A} \frac{c_j^+}{\sum_{k=1}^n c_k^+} \Big(z_j - \frac{\sum_{k=1}^n z_k c_k^+}{\sum_{k=1}^n c_k^+} \Big)$. The terms $\Gamma_j(\mathbf{c}^+)$ are uniformly bounded:

$0 \leqslant \Gamma(c_j^+) \leqslant \dfrac{CZ}{N_A}$, where $Z = \sum_{i=1}^{n} |z_i|$, which allows to use the Schauder–Tikhonov fixed point theorem. If constraints (5a) and (5b) hold, then $\Gamma_j(\mathbf{c}^+) = \Upsilon_j(\mathbf{c})$ and $\Gamma(\mathbf{c}^+) = \Upsilon(\mathbf{c})$ and the original and the reduced formulations coincide.

Theorem 1 (Existence of a weak solution of the reduced problem) *Let the growth conditions for reactions on the boundary* (6) *hold and let the coefficient matrices A and $m_i D^{ij}$ be spd-matrices. Then there exists a weak solution of the reduced problem.*

Lemma 2 (Volume balance) *Under assumptions on the boundary* (7) *and the weak assumption of the diffusivity matrices* (9) *the volume constraint $\sum_{i=1}^{n} c_i = C$ is satisfied a.e. on $(0,T) \times (Q \cup \omega)$.*

Lemma 3 (Weak maximum principle) *Under assumptions on the data* (8) *and* (10) *we have the positive solution $c_i \geqslant 0$ a.e. on $(0,T) \times (Q \cup \omega)$ for $i = 1, \ldots, n$.*

Lemma 4 (Equivalence of formulations) *Under assumptions made in Lemmas 2 and 3 the complete and the reduced problems are equivalent.*

Theorem 5 (Well–posedness of generalized Poisson–Nernst–Planck system) *Let assumptions* (6)–(8) *on the nonlinear boundary terms hold.*

(1) *If the weak assumption on diffusivity matrices holds, then there exists a weak solution of the problem. By continuity, $\mathbf{c} > 0$ locally for small $t > 0$.*
(2) *If additionally the strong assumption on diffusivity matrices holds, then $\mathbf{c} \geqslant 0$ globally for $T > 0$.*

A weak solution satisfies the a priori estimates

$$||\varphi||^2_{L^\infty(0,T;H^1(Q)\times H^1(\omega))} \leqslant K_\varphi, \tag{12}$$

$$||\boldsymbol{c}||^2_{L^\infty(0,T;L^2(Q)\times L^2(\omega))} + ||\boldsymbol{c}||^2_{L^2(0,T;H^1(Q)\times H^1(\omega))} \leqslant K_c + \gamma_c K_\varphi. \tag{13}$$

Under additional assumption on the regularity of the electrostatic potential φ as well as injectivity and continuity of the nonlinear boundary fluxes $g_i(\hat{\mathbf{c}}, \hat{\varphi})$, a weak solution of the generalized PNP problem is unique.

We define the entropy and the function of dissipation as follows:

$$S(t) := -k_B N_A \sum_{i=1}^{n} \int_{Q\cup\omega} c_i \ln(\beta_i c_i)\, dx \text{ and } \mathcal{D}(t) := -\frac{dS}{dt} = k_B N_A \sum_{i=1}^{n} \int_{Q\cup\omega} \frac{\partial c_i}{\partial t} \ln(\beta_i c_i)\, dx.$$

The dissipation inequality $\mathcal{D} \geqslant 0$ can be assured under additional assumptions $m_i D^{ij} = \underline{d}\delta_{ij} I$, $A = \underline{a} I$, $\sum_{i=1}^{n} z_i c_i^D = 0$ and $c_i^D = 1/\beta_i$ on $\partial\Omega$ and with a special choice of the boundary functions g and $g_i(\hat{\mathbf{c}}, \hat{\varphi})$.

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