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A gradient structure for systems coupling reaction-diffusion effects in bulk and interfaces

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Abstract

We derive gradient-flow formulations for systems describing drift-diffusion processes of a finite number of species which undergo mass-action type reversible reactions. Our investigations cover heterostructures, where material parameter may depend in a nonsmooth way on the space variable. The main results concern a gradient flow formulation for electro-reaction-diffusion systems with active interfaces permitting drift-diffusion processes and reactions of species living on the interface and transfer mechanisms allowing bulk species to jump into an interface or to pass through interfaces.

The gradient flows are formulated in terms of two functionals: the free energy and the dissipation potential. Both functionals consist of a bulk and an interface integral. The interface integrals determine the interface dynamics as well as the self-consistent coupling to the model in the bulk. The advantage of the gradient structure is that it automatically generates thermodynamically consistent models.

1 Introduction and gradient formulations

In several papers by Otto (see [JKO98, Ott98, Ott01]) it was demonstrated that certain diffusion problems can be interpreted as gradient flows with respect to the free energy or the entropy as a driving functional. In [Mie11] this concept is generalized firstly to processes where reactions between different species take place and secondly to processes with a temperature coupling and thirdly to processes where an electrostatic interaction has to be taken into account. In the present paper we first recall the gradient-flow formulations for electro-reaction-diffusion problems without active interfaces (see Section 2). In difference to [Mie11], our considerations take into account heterostructures, where material parameters depend nonsmoothly on the space variable. In the next step we generalize this concept to the situation that at interfaces in the heterostructure there exist extra kinetic processes, namely drift-diffusion, reactions and transfer mechanisms for bulk species (see Section 3). The closing section is devoted to examples of electro-reaction-diffusion problems with such active interfaces, having in mind future applications in photovoltaics, especially in thin-film solar cells (see e.g. [SLH10]).

The setting of gradient flows can be described as follows (see e.g. [Mie11]): For a linear state space $\boldsymbol{Z}$ we consider a dissipation functional $\Psi(\boldsymbol{z},\dot{\boldsymbol{z}}) : T\boldsymbol{Z} \to [0,\infty]$. For each $\boldsymbol{z}$ the functional $\Psi(z,.) : T_{\boldsymbol{z}}\boldsymbol{Z} \to [0,\infty]$ is assumed to be convex, lower semicontinuous, and has to fulfill $\Psi(\boldsymbol{z},0) = 0$. For gradient flows (in the classical or narrow sense) the dissipation potential $\Psi(z,\cdot)$ is assumed to be a quadratic form, e.g. $\Psi(\boldsymbol{z},\dot{\boldsymbol{z}}) = \frac{1}{2}\langle \boldsymbol{G}(z)\dot{\boldsymbol{z}},\dot{\boldsymbol{z}}\rangle$, where $\boldsymbol{G} = \boldsymbol{G}^* \geq 0$ plays the role of a Riemannian metric tensor.

For a given energy functional $\mathcal{F} : \boldsymbol{Z} \to \mathbb{R} \cup \{+\infty\}$ the generalized gradient flow is given by

$$0 \in \partial_{\dot{\boldsymbol{z}}}\Psi(\boldsymbol{z},\dot{\boldsymbol{z}}) + D\mathcal{F}(\boldsymbol{z}) \text{ in } T^*_{\boldsymbol{z}}\boldsymbol{Z} \sim \boldsymbol{Z}^*. \tag{1.1}$$

An equivalent formulation can be obtained using the Legendre transform and the dual dissipation functional $\Psi^* : T^*\boldsymbol{Z} \to [0,\infty]$,

$$\Psi^*(\boldsymbol{z};\cdot) = \mathcal{L}[\Psi(\boldsymbol{z},\cdot)], \quad \Psi^*(\boldsymbol{z};\boldsymbol{\eta}) = \sup_{\boldsymbol{v}\in\boldsymbol{Z}} \Big\{ \langle \boldsymbol{\eta}, \boldsymbol{v}\rangle - \Psi(\boldsymbol{z},\boldsymbol{v}) \Big\}.$$

Then (1.1) can be written equivalently as rate equation

$$\dot{\boldsymbol{z}} = \partial_{\boldsymbol{\eta}} \Psi^*(\boldsymbol{z}; -D\mathcal{F}(\boldsymbol{z})). \tag{1.2}$$

Using (1.1), (1.2) and the classical Legendre equivalence (where $\mathcal{J}$ is a general lower semicontinuous, convex functional)

$$\boldsymbol{\eta} \in \partial\mathcal{J}(\boldsymbol{v}) \quad \Longleftrightarrow \quad \boldsymbol{v} \in \partial\mathcal{J}^*(\boldsymbol{\eta}) \quad \Longleftrightarrow \quad \mathcal{J}(\boldsymbol{v}) + \mathcal{J}^*(\boldsymbol{\eta}) = \langle \boldsymbol{\eta}, \boldsymbol{v}\rangle$$

the energy balance can be given in different formulations

$$\begin{aligned} \mathcal{F}(\boldsymbol{z}(0)) - \mathcal{F}(\boldsymbol{z}(t)) &= \int_0^t \langle -D\mathcal{F}(\boldsymbol{z}), \dot{\boldsymbol{z}}\rangle \,\mathrm{d}s = \int_0^t \langle \partial_{\dot{\boldsymbol{z}}}\Psi(\boldsymbol{z},\dot{\boldsymbol{z}}), \dot{\boldsymbol{z}}\rangle \,\mathrm{d}s \\ &= \int_0^t \big(\Psi(\boldsymbol{z},\dot{\boldsymbol{z}}) + \Psi^*(\boldsymbol{z}; -D\mathcal{F}(\boldsymbol{z})\big)\,\mathrm{d}s \; = \; \int_0^t \langle -D\mathcal{F}(\boldsymbol{z}), \partial_{\boldsymbol{\eta}}\Psi^*(\boldsymbol{z}; -D\mathcal{F}(\boldsymbol{z}))\rangle \,\mathrm{d}s. \end{aligned}$$

Since the right hand sides express the dissipated energy, Ψ is called the dissipation potential and Ψ^* the dual dissipation potential. In the applications of our paper we consider isothermal systems such that the free energy will play the role of the driving functional.

In the rest of this work we will restrict ourselves to the case of true gradient flows, where $\Psi(\boldsymbol{z},\cdot)$ and hence also $\Psi^*(\boldsymbol{z},\cdot)$ are quadratic forms. Usually, we write the gradient system in the dual form and use the representation

$$\Psi^*(\boldsymbol{z},\boldsymbol{\eta}) = \frac{1}{2}\langle \boldsymbol{\eta}, \boldsymbol{K}(\boldsymbol{z})\boldsymbol{\eta}\rangle,$$

where the operator $\boldsymbol{K} = \boldsymbol{K}^* \geq 0$ maps from $\boldsymbol{Z}^*$ to $\boldsymbol{Z}$ (or some subspaces). The dual form is easier, since we are interested in the case that $\boldsymbol{K}$ is not invertible, which allows for conserved quantities. Our gradient system takes the form

$$\dot{\boldsymbol{n}} = D_{\boldsymbol{\eta}}\Psi^*(\boldsymbol{n}; -D\mathcal{F}(\boldsymbol{n})) = -\boldsymbol{K}(\boldsymbol{n})D\mathcal{F}(\boldsymbol{n}),$$

where $\boldsymbol{n}$ denotes the vector of densities of the species and $\boldsymbol{\eta} = D\mathcal{F}(\boldsymbol{n})$ represents the corresponding thermodynamic force being conjugate to $\boldsymbol{n}$, which is called the vector of the chemical potentials. The operator $\boldsymbol{K}$ can be seen as a generalization of the symmetric Onsager matrix. In this setting the functional $\mathcal{F}$ becomes decreasing and the expression $\Psi(\boldsymbol{n},\dot{\boldsymbol{n}}) + \Psi^*(\boldsymbol{n}; -D\mathcal{F}(\boldsymbol{n}))$ describes the energy dissipation. The aim in the paper is to find suitable functionals $\mathcal{F}$ and potentials Ψ such that electro-reaction-diffusion systems without and with active interfaces fit into this formalism and can be written as gradient flows.

We recall that in [Mie11] it was shown that $\boldsymbol{K}$ for electro-reaction diffusion systems can be written in the form

$$\boldsymbol{K}(\boldsymbol{n})\boldsymbol{\eta} = -\operatorname{div}\big(\boldsymbol{M}(\boldsymbol{n})\nabla\boldsymbol{\eta}\big) + \boldsymbol{H}(\boldsymbol{n})\boldsymbol{\eta},$$

where the tensor $\boldsymbol{M}$ contains the mobilities for the bulk diffusion, while the matrix $\boldsymbol{H}(\boldsymbol{n})$ contains the rate coefficients for the reactions.

In this paper we model the interaction between a bulk system and an interface system by extending the above ideas to functionals given as a sum of a bulk and an interface term. We consider an interface Γ which lies between the material Ω. By Γ^+ and Γ^- we denote the two surfaces that are obtained by approaching Γ from above and below, see Section 3 for more details. We denote by $\boldsymbol{n} \in\,]0,\infty[^I$ and by $\boldsymbol{n}_\Gamma \in\,]0,\infty[^{I_\Gamma}$ the vectors of the densities on the bulk and the interface, respectively. The bulk-interface energy $\mathcal{F}_{\mathrm{BI}}$ is typically given in the form

$$\mathcal{F}_{\mathrm{BI}}(\boldsymbol{n},\boldsymbol{n}_\Gamma) = \int_{\Omega\setminus\Gamma}\sum_{i=1}^{I} n_i\big(\log(\tfrac{n_i}{n_{*i}}){-}1\big)\,\mathrm{d}x + \int_\Gamma \sum_{i=1}^{I_\Gamma} n_{\Gamma i}\big(\log(\tfrac{n_{\Gamma i}}{n_{\Gamma * i}}){-}1\big)\,\mathrm{d}a. \tag{1.3a}$$

One typical form of the dual dissipation potential is given by

$$\begin{aligned}\Psi^*_{\mathrm{BI}}(\boldsymbol{n},\boldsymbol{n}_\Gamma;\boldsymbol{\eta},\boldsymbol{\eta}_\Gamma) = {}&\\ \int_{\Omega\setminus\Gamma}&\tfrac12\nabla\boldsymbol{\eta}{:}\boldsymbol{M}_{\mathrm{bulk}}(\boldsymbol{n}){:}\nabla\boldsymbol{\eta} + \tfrac12\boldsymbol{\eta}\cdot\boldsymbol{H}_{\mathrm{bulk}}(\boldsymbol{n})\boldsymbol{\eta}\,\mathrm{d}x + \int_\Gamma \tfrac12\nabla_\Gamma\boldsymbol{\eta}_\Gamma{:}\boldsymbol{M}_\Gamma(\boldsymbol{n}_\Gamma){:}\nabla_\Gamma\boldsymbol{\eta}_\Gamma\,\mathrm{d}a\\ +\int_\Gamma&\tfrac12(B^+\boldsymbol{\eta}^+{+}B^-\boldsymbol{\eta}^-{+}C\boldsymbol{\eta}_\Gamma)\cdot\widetilde{\boldsymbol{H}}_\Gamma(\boldsymbol{n}_+,\boldsymbol{n}_-,\boldsymbol{n}_\Gamma)(B^+\boldsymbol{\eta}^+{+}B^-\boldsymbol{\eta}^-{+}C\boldsymbol{\eta}_\Gamma)\,\mathrm{d}a.\end{aligned} \tag{1.3b}$$

Here $\boldsymbol{n}^\pm$ and $\boldsymbol{\eta}^\pm$ are the traces of $\boldsymbol{n}$ and $\boldsymbol{\eta}$ on $\Gamma^\pm$, respectively, and ∇_Γ denotes the tangential gradient on Γ. The matrix $\widetilde{\boldsymbol{H}}_\Gamma$ models the transfer between the Γ^+, Γ, and Γ^- as well as reactions in Γ, while the coefficient matrices $B^\pm$ and C contain stochiometric coefficients.

Applying the abstract gradient form (1.2), $\boldsymbol{M}_{\mathrm{bulk}}$ and $\boldsymbol{H}_{\mathrm{bulk}}$ give rise to the reaction-diffusion system in the bulk

$$\dot{\boldsymbol{n}} = \operatorname{div}\big(\boldsymbol{M}_{\mathrm{bulk}}(\boldsymbol{n})\nabla\boldsymbol{\eta}\big) - \boldsymbol{H}_{\mathrm{bulk}}(\boldsymbol{n})\boldsymbol{\eta},\quad \text{where } \boldsymbol{\eta} = (\log n_i - \log n_{*i})_{i=1,\dots,I}. \tag{1.4a}$$

In the interface Γ we have diffusion and reactions via $\boldsymbol{M}_\Gamma$ and $\widetilde{\boldsymbol{H}}_\Gamma$, namely

$$\dot{\boldsymbol{n}}_\Gamma = \operatorname{div}_\Gamma\big(\boldsymbol{M}_\Gamma(\boldsymbol{n}_\Gamma)\nabla_\Gamma\boldsymbol{\eta}_\Gamma\big) - C^{\mathsf{T}}\widetilde{\boldsymbol{H}}_\Gamma(\ldots)(B^+\boldsymbol{\eta}^+{+}B^-\boldsymbol{\eta}^-{+}C\boldsymbol{\eta}_\Gamma). \tag{1.4b}$$

In addition, we obtain interface conditions on $\Gamma^\pm$ as follows:

$$\nu^\pm\cdot\boldsymbol{M}_{\mathrm{bulk}}(\boldsymbol{n}_\pm)\eta^\pm = (B^\pm)^{\mathsf{T}}\widetilde{\boldsymbol{H}}_\Gamma(\ldots)(B^+\boldsymbol{\eta}^+{+}B^-\boldsymbol{\eta}^-{+}C\boldsymbol{\eta}_\Gamma)\ \text{ on } \Gamma^\pm. \tag{1.4c}$$

We refer to Theorem 3.1 for the proof in an even more general setting.

Thus, the gradient system generated by $\mathcal{F}$ and Ψ^* defined in (1.3) defines in a natural way the coupled system (1.4) of partial differential equations. Our paper will follow these lines for the more general case of electro-reaction-diffusion systems where the particles may be charged. The gradient of associated electrostatic potential ϕ induced by the bulk densities $\boldsymbol{n}$ and the interface densities $\boldsymbol{n}_\Gamma$ will generate an additional drift term, which still can be formulated as gradient systems, see [Mie11].

The plan of the paper is as follows. In Section 2 we recall the bulk theory for electro-reaction-diffusion system as established in [Mie11], but generalize it to the case of heterostructures, where the equilibrium densities $\boldsymbol{n}_*$ may depend nonsmoothly on the material point $x \in \Omega$. In Section 3 we then discuss the generalization to systems, where new species with density vector $\boldsymbol{n}_\Gamma$ are confined to an active interface. We discuss the interaction mechanisms as well as the detailed balance conditions needed to obtain the desired gradient structure. In Section 4 we discuss several examples that highlight different aspects of the general theory. We first treat a scalar diffusion equation with bulk-interface interaction. Second we study reaction-diffusion systems, where on the interface reactions happen which need species from the bulk. Finally, we provide a semiconductor model for a solar cell, where charged and neutral traps in an interface influence the motion of electrons and holes.

We emphasize that the modeling of electro-reaction-diffusion systems via gradient structures is an alternative to the modeling via the mass-action formalism involving the detailed-balance or Wegscheider conditions. While our theory of gradient structures is restricted to closed systems, it has the advantage that the derived systems are automatically thermodynamically correct giving the Onsager form $\dot{\boldsymbol{n}} = -\boldsymbol{K}(\boldsymbol{n})D\mathcal{F}_{\mathrm{BI}}(\boldsymbol{n})$, which is derived from the free energy $\mathcal{F}_{\mathrm{BI}}$ and the dual dissipation potential $\Psi^*_{\mathrm{BI}} : \boldsymbol{\eta} \mapsto \frac{1}{2}\langle \boldsymbol{\eta}, \boldsymbol{K}(\boldsymbol{n})\boldsymbol{\eta}\rangle$. For modeling the two functionals $\mathcal{F}_{\mathrm{BI}}$ and Ψ^*_{BI} determine how many coefficients can be chosen independently, as the resulting systems will always be thermodynamically correct. This is helpful for complicated electro-reaction-diffusion systems with bulk-interface interactions such as the solar-cell model in Subsection 4.3.

In contrast, the direct modeling of electro-reaction-diffusion systems [DeM84, ÉrT89, GGH96] via reactions of mass-action type satisfying the detailed-balance conditions is more flexible for open systems, where the gradient structure is lost but thermodynamic correctness can still be present.

2 Electro-reaction-diffusion systems

The abstract framework of gradient structures for electro-reaction-diffusion systems will be derived combining results concerning generalized gradient flows obtained for reaction-diffusion systems in [Mie11, Subsec. 3.3] and some generalization of such results for the van Roosbroeck system (see [Mie11, Subsec. 4.1]). The point is to show that for closed systems the modeling via gradient structures is equivalent to to the modeling via reactions of mass-action type satisfying the detailed balance conditions (or equivalently Wegscheider's cyclicity condtions).

Here we additionally generalize the setting to heterostructures, where material properties may depend nonsmoothly on $x \in \Omega$. But we don't indicate the space dependency in each formula explicitely. At the end of this section we summarize which of the occuring quantities can depend nonsmoothly on x. We start with some notation.

In a domain $\Omega \subset \mathbb{R}^N$ we consider I different species X_i with densities n_i, $\boldsymbol{n} = (n_1, \ldots, n_I)$. These species are reacting according to the mass action law, i.e. we take into account the reactions

$$\alpha_1^r X_1 + \cdots + \alpha_I^r X_I \underset{k_{\mathrm{r}}^r}{\overset{k_{\mathrm{f}}^r}{\rightleftharpoons}} \beta_1^r X_1 + \cdots + \beta_I^r X_I,$$

where $r = 1, \ldots, R$ is the number of possible reactions, $\boldsymbol{\alpha}^r = (\alpha_1^r, \ldots, \alpha_I^r)$, $\boldsymbol{\beta}^r \in \mathbb{N}_0^I$ are the vectors of stoichiometric coefficients, and k_{f}^r and k_{r}^r the positive *forward* and *reverse* rate coefficients, which may depend on $\boldsymbol{n}$ and x as well.

To write the reaction terms we use the abbreviation $\boldsymbol{n}^{\boldsymbol{\alpha}^r} = n_1^{\alpha_1^r} \ldots n_I^{\alpha_I^r}$. According to [FeH77, Grö83, ÉrT89, VlR09] the source term due to the considered reactions in the rate equation reads

$$\dot{\boldsymbol{n}} = \boldsymbol{R}(\boldsymbol{n}) = -\sum_{i=1}^{R} \big(k_{\mathrm{f}}^r(\boldsymbol{n})\boldsymbol{n}^{\boldsymbol{\alpha}^r} - k_{\mathrm{r}}^r(\boldsymbol{n})\boldsymbol{n}^{\boldsymbol{\beta}^r}\big)(\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r).$$

We introduce the stoichiometric subspace $\mathcal{S}$ and its orthogonal complement $\mathcal{S}^\perp$,

$$\mathcal{S} := \operatorname{span}\{\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r |\ r = 1, \ldots, R\} \subset \mathbb{R}^I, \quad \mathcal{S}^\perp := \{\kappa \in \mathbb{R}^I |\ \kappa \cdot \rho = 0 \text{ for all } \rho \in \mathcal{S}\}.$$

We associate to each species X_i a charge number $q_i \in \mathbb{Z}$ and write $\boldsymbol{q} = (q_1, \ldots, q_I)$. It is reasonable to assume that all considered reactions are charge conserving, which means that $\boldsymbol{q} \in \mathcal{S}^\perp$. Furthermore, concerning the reaction system we assume that the rate coefficients for the forward and backward reaction (almost everywhere) in Ω have the form

$$k_{\mathrm{r}}^r(\boldsymbol{n}) = k_0^r k_{\mathrm{f}}^r(\boldsymbol{n})$$

with k_0^r not depending on the state $\boldsymbol{n}$, but possibly depending on $x \in \Omega$. The formulation using the possibly space depending $\boldsymbol{n}_*$ enables us to treat spatial inhomogeneities, especially it is possible to incorporate heterostructures that are of fundamental importance in semiconductor design, see [BHK03, BGH05].

The crucial assumption is the *detailed balance condition* to be fulfilled. This means that there exists a positive equilibrium density vector $\boldsymbol{n}_* \in\,]0, \infty[^I$ such that

$$\boldsymbol{n}_*^{\boldsymbol{\alpha}^r} = k_0^r \boldsymbol{n}_*^{\boldsymbol{\beta}^r} \text{ for } r = 1, \ldots, R \iff A \,\mathbf{log}\, \boldsymbol{n}_* = (\log k_0^r)_{r=1,\ldots,R}, \tag{2.1}$$

where the matrix $A \in \mathbb{Z}^{R \times I}$ has the row vectors $\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r \in \mathbb{Z}^I$. These conditions are also called *Wegscheider's cyclicity conditions* (see e.g. [VlR09, Weg02]). If the vector

$(\log k_0^r)_{r=1,\ldots,R}$ on the right-hand side of the system of linear equations for $\mathbf{log}\,\boldsymbol{n}_*$ in (2.1) is orthogonal to all solutions of the homogeneous adjoint system (a.e. on Ω), then the existence of a positive solution $\boldsymbol{n}_*$ is guaranteed.

In electro-chemical systems the considered species may carry charges, that generate an electrostatic potential $\phi_{\boldsymbol{n}}$, which is the unique solution to the Poisson equation

$$\begin{aligned} &-\operatorname{div}(\varepsilon\,\nabla\phi) = d + \boldsymbol{q}\cdot\boldsymbol{n} \text{ in } \Omega,\\ &\phi = \phi_{\mathrm{D}ir} \text{ on } \Gamma_{\mathrm{D}} \text{ and } \varepsilon\,\nabla\phi\cdot\nu = 0 \text{ on } \Gamma_{\mathrm{N}}. \end{aligned} \tag{2.2}$$

Here ε is the dielectric permittivity (tensor) and d represents some fixed charge density, the doping profile. Both quantities may depend nonsmoothly on the space variable. Due to this electrostatic potential the flux density j_i for the charged species contains in addition to the diffusive part (Fick's law) a drift part,

$$j_i = -M_i(\boldsymbol{n})\nabla\big(\log\frac{n_i}{n_{*i}} + q_i\phi_{\boldsymbol{n}}\big), \quad i = 1,\ldots,I.$$

Here $M_i(\boldsymbol{n})$ are symmetric positive semidefinite $N\times N$ matrices being allowed to depend in a nonsmooth way on x. The simplest realization of $M_i(\boldsymbol{n})$ is $M_i(\boldsymbol{n}) = m_i n_i$ where m_i is a scalar diffusion coefficient. The electro-reaction-diffusion system now reads as the coupled system of the Poisson equation (2.2) and continuity equations for all species

$$\begin{aligned} &\frac{\partial n_i}{\partial t} + \operatorname{div} j_i = R_i(\boldsymbol{n}) \quad \text{in } \Omega,\\ &j_i\cdot\nu = 0 \quad \text{on } \partial\Omega, \quad i = 1,\ldots,I. \end{aligned} \tag{2.3}$$

Testing system (2.3) by a constant vector $\boldsymbol{p}\in\mathcal{S}^\perp$ we find for the functional

$$\mathcal{P}_{\boldsymbol{p}}(\boldsymbol{n}) := \int_\Omega \boldsymbol{p}\cdot\boldsymbol{n}\,\mathrm{d}x$$

that all solutions $(\boldsymbol{n},\phi_{\boldsymbol{n}})$ to (2.2), (2.3) satisfy the identity

$$\mathcal{P}_{\boldsymbol{p}}(\boldsymbol{n}(t)) = \mathcal{P}_{\boldsymbol{p}}(\boldsymbol{n}(0)) \quad \text{for all } t\ge 0.$$

In other words, each vector $\boldsymbol{p}\in\mathcal{S}^\perp$ defines a conserved quantity $\mathcal{P}_{\boldsymbol{p}}(\boldsymbol{n})$.

For a multi-species Boltzmann-distributed system of charged species the free energy consists of an electrostatic part and a chemical part:

$$\mathcal{F}(\boldsymbol{n}) := \int_\Omega \Big\{\frac{1}{2}\nabla\phi_{\boldsymbol{n}}\cdot(\varepsilon\nabla\phi_{\boldsymbol{n}}) + \sum_{i=1}^I n_i(\log\frac{n_i}{n_{*i}} - 1)\Big\}\,\mathrm{d}x, \tag{2.4}$$

where the electrostatic potential $\phi_{\boldsymbol{n}}$ is the solution to the Poisson equation (2.2). By differentiation we obtain

$$D\mathcal{F}(\boldsymbol{n}) = \Big(\log\frac{n_i}{n_{*i}} + q_i\phi_{\boldsymbol{n}}\Big)_{1=1,\ldots,I} =: \boldsymbol{\eta},$$

For this relation one additionally has to use that $\phi_{\boldsymbol{n}}$ solves the Poisson equation (2.2) and depends affinely on $\boldsymbol{n}$, see [GGH96, GlH97, AGH02] or the proof of Theorem 3.1.

Let $\boldsymbol{n}_0$ be any given vector of initial densities. Minimizing $\mathcal{F}$ as given in (2.4) under the constraint $\mathbb{Q}\int_\Omega(\boldsymbol{n}-\boldsymbol{n}_0)\,\mathrm{d}x = 0$ (where $\mathbb{Q}:\mathbb{R}^I\to\mathbb{R}^I$ is any projection onto $\mathcal{S}^\perp$), we obtain, under suitable technical assumptions (cf. [GlH97, GGH96], arguing with the conjugate functional of the free energy functional, see [GGH96, Section 3]), the existence of a unique minimizer $\boldsymbol{n}_{\mathrm{eq}}^{\boldsymbol{n}_0}$ of $\mathcal{F}$ subject to the above constraint. We call $\boldsymbol{n}_{\mathrm{eq}}^{\boldsymbol{n}_0}$ the *thermodynamic equilibrium*. According to the Lagrange formalism for constrained minimization it fulfills

$$\mathrm{D}\mathcal{F}(\boldsymbol{n}_{\mathrm{eq}}^{\boldsymbol{n}_0}) = \Big(\log\frac{n_{\mathrm{eq}\,i}^{\boldsymbol{n}_0}}{n_{*i}} + q_i\phi_{\boldsymbol{n}_{\mathrm{eq}}^{\boldsymbol{n}_0}}\Big)_{1=1,\dots,I} \equiv \boldsymbol{\eta}_{\mathrm{eq}}\in\mathcal{S}^\perp, \quad \mathbb{Q}\int_\Omega(\boldsymbol{n}_{\mathrm{eq}}^{\boldsymbol{n}_0}-\boldsymbol{n}_0)\,\mathrm{d}x = 0, \tag{2.5}$$

where $\phi_{\boldsymbol{n}_{\mathrm{eq}}^{\boldsymbol{n}_0}}$ is the unique solution to (2.2) with $\boldsymbol{n}_{\mathrm{eq}}^{\boldsymbol{n}_0}$ in the right-hand side.

To model the dynamics of the system we use the primary variables $\boldsymbol{n}$ and the dual variables $\boldsymbol{\eta}$ and define the dual dissipation potential Ψ^* consisting of a mobility part giving rise to the diffusion and drift and a reactive part. The latter is associated to the reaction processes and takes the form

$$\begin{aligned}
&\psi^*(\boldsymbol{n};\boldsymbol{\eta}) := \frac{1}{2}\boldsymbol{\eta}\cdot\boldsymbol{H}(\boldsymbol{n})\boldsymbol{\eta} \quad\text{with}\\
&\boldsymbol{H}(\boldsymbol{n}) := \sum_{r=1}^R k_{\mathrm{f}}^r(\boldsymbol{n})\,\boldsymbol{n}_*^{\boldsymbol{\alpha}^r}\,\Lambda\big(\frac{\boldsymbol{n}^{\boldsymbol{\alpha}^r}}{\boldsymbol{n}_*^{\boldsymbol{\alpha}^r}},\frac{\boldsymbol{n}^{\boldsymbol{\beta}^r}}{\boldsymbol{n}_*^{\boldsymbol{\beta}^r}}\big)\,(\boldsymbol{\alpha}^r-\boldsymbol{\beta}^r)\otimes(\boldsymbol{\alpha}^r-\boldsymbol{\beta}^r),
\end{aligned}\tag{2.6}$$

where the function Λ is given by

$$\Lambda(x,y) = \begin{cases}\frac{x-y}{\log x-\log y} & \text{for } x\neq y,\\ y & \text{for } x=y.\end{cases}\tag{2.7}$$

Because of $\Lambda(x,y)>0$ for $x,y>0$ the matrix $\boldsymbol{H}\in\mathbb{R}^{I\times I}$ is symmetric and positive semi-definite. For positive $k_{\mathrm{f}}^r(\boldsymbol{n})$, $r=1,\dots,R$, we have $(H(\boldsymbol{n})\boldsymbol{\eta})\cdot\boldsymbol{\eta}=0$ if and only if $\boldsymbol{\eta}\in\mathcal{S}^\perp$. For $\boldsymbol{p}\in\mathcal{S}^\perp$ we have $\boldsymbol{H}(\boldsymbol{n})\boldsymbol{p}=0$, which implies

$$\psi^*(\boldsymbol{n};\boldsymbol{\eta}+\boldsymbol{p}) = \psi^*(\boldsymbol{n};\boldsymbol{\eta}) \quad \text{for all } \boldsymbol{p}\in\mathcal{S}^\perp. \tag{2.8}$$

Moreover, using $\boldsymbol{q}\in\mathcal{S}^\perp$ again $\boldsymbol{\eta}=\mathrm{D}\mathcal{F}(\boldsymbol{n})$ satisfies

$$(\boldsymbol{\alpha}^r-\boldsymbol{\beta}^r)\cdot\boldsymbol{\eta} = \log\big(\frac{\boldsymbol{n}^{\boldsymbol{\alpha}^r}}{\boldsymbol{n}_*^{\boldsymbol{\alpha}^r}}\big) - \log\big(\frac{\boldsymbol{n}^{\boldsymbol{\beta}^r}}{\boldsymbol{n}_*^{\boldsymbol{\beta}^r}}\big) + (\boldsymbol{\alpha}^r-\boldsymbol{\beta}^r)\cdot\boldsymbol{q}\,\phi_{\boldsymbol{n}} = \log\big(\frac{\boldsymbol{n}^{\boldsymbol{\alpha}^r}}{\boldsymbol{n}_*^{\boldsymbol{\alpha}^r}}\big) - \log\big(\frac{\boldsymbol{n}^{\boldsymbol{\beta}^r}}{\boldsymbol{n}_*^{\boldsymbol{\beta}^r}}\big),$$

and we obtain

$$\begin{aligned}
&\mathrm{D}_\eta\psi^*(\boldsymbol{n};-\mathrm{D}\mathcal{F}(\boldsymbol{n})) = \boldsymbol{H}(\boldsymbol{n})(-\boldsymbol{\eta})\\
&=\sum_{r=1}^R k_{\mathrm{f}}^r(\boldsymbol{n})\boldsymbol{n}_*^{\boldsymbol{\alpha}^r}\Lambda\big(\frac{\boldsymbol{n}^{\boldsymbol{\alpha}^r}}{\boldsymbol{n}_*^{\boldsymbol{\alpha}^r}},\frac{\boldsymbol{n}^{\boldsymbol{\beta}^r}}{\boldsymbol{n}_*^{\boldsymbol{\beta}^r}}\big)\big(\log\big(\frac{\boldsymbol{n}^{\boldsymbol{\alpha}^r}}{\boldsymbol{n}_*^{\boldsymbol{\alpha}^r}}\big)-\log\big(\frac{\boldsymbol{n}^{\boldsymbol{\beta}^r}}{\boldsymbol{n}_*^{\boldsymbol{\beta}^r}}\big)\big)(\boldsymbol{\beta}^r-\boldsymbol{\alpha}^r) \;=\; \boldsymbol{R}(\boldsymbol{n}).
\end{aligned}$$

Thus, the reaction terms are modeled correctly.

The overall dual dissipation functional Ψ^* containing drift, diffusion and reaction effects is postulated to have the form

$$\Psi^*(\boldsymbol{n};\boldsymbol{\eta}) = \int_\Omega \Big\{ \sum_{i=1}^{I} \frac{1}{2}\nabla\eta_i(x)\cdot(M_i(\boldsymbol{n})\nabla\eta_i(x)) + \psi^*(\boldsymbol{n}(x);\boldsymbol{\eta}(x))\Big\}\,\mathrm{d}x, \tag{2.9}$$

where ψ^* is given in (2.6) and $M_i(\boldsymbol{n})$ are symmetric positive semidefinite $N\times N$ matrices. In the simplest case we have $M_i(\boldsymbol{n}) = m_i n_i$ with a scalar diffusion coefficient m_i, $i = 1,\ldots,I$. However, we may also generalize to cases allowing for cross-diffusion by choosing a fourth-order tensor $\mathbb{M}(\boldsymbol{n})$ acting on the gradient $\nabla\boldsymbol{\eta}\in\mathbb{R}^{I\times N}$.

Since $\mathrm{D}\mathcal{P}_{\boldsymbol{p}}(\boldsymbol{n}) = \boldsymbol{p}\in\mathcal{S}^\perp$ are constants and since (2.8) is fulfilled we establish the identity

$$\Psi^*\big(\boldsymbol{n};-\mathrm{D}\mathcal{F}(\boldsymbol{n})+\mathrm{D}\mathcal{P}_{\boldsymbol{p}}(\boldsymbol{n})\big) = \Psi^*(\boldsymbol{n};-\mathrm{D}\mathcal{F}(\boldsymbol{n})) \quad \text{for all } \boldsymbol{p}\in\mathcal{S}^\perp.$$

Moreover, under the simplifying assumption that $k^r_{\mathrm{f}}(\boldsymbol{n}) > 0$ and $M_i(\boldsymbol{n})$ are positive definite for all $\boldsymbol{n}\in(0,\infty)^I$ we have $\Psi^*(\boldsymbol{n};-\mathrm{D}\mathcal{F}(\boldsymbol{n})) = 0$ if and only if $\mathrm{D}\mathcal{F}(\boldsymbol{n})$ is a constant vector lying in $\mathcal{S}^\perp$.

Since the derivative of Ψ^* with respect to the second argument is

$$\mathrm{D}_{\boldsymbol{\eta}}\Psi^*(\boldsymbol{n};\mathrm{D}\mathcal{F}(\boldsymbol{n})) = -\Big(\mathrm{div}\,(M_i(\boldsymbol{n})\nabla\eta_i) + R_i(\boldsymbol{n})\Big)_{i=1,\ldots,I},$$

our choice of the energy functional $\mathcal{F}$ and the dual dissipation potential Ψ^* gives the gradient system for $\boldsymbol{n}$ in the dual formulation

$$\frac{\partial\boldsymbol{n}}{\partial t} = -\mathrm{D}_{\boldsymbol{\eta}}\Psi^*(\boldsymbol{n};\mathrm{D}\mathcal{F}(\boldsymbol{n})),$$

which exactly corresponds to the continuity equations (2.3). And the validity of the Poisson equation (2.2) during the time being is incorporated in the definition of the free energy. Thus, we have found a formulation of the electro-reaction-diffusion system (2.2), (2.3) as a gradient flow.

Remark 2.1 (Heterostructures) *We recall that our considerations cover the situation of heterostructures, where the physical parameters are allowed to depend in a nonsmooth way on the space variable. Now, at the end of our argumentation in this section we once more collect all the relevant space dependent quantities. So the reaction rate coefficients* $k^r_f(\boldsymbol{n})$, $k^r_r(\boldsymbol{n})$, k^r_0, *the quantities in the Poisson equation* ε *and* d *as well as the matrices* $M_i(\boldsymbol{n})$ *are allowed to have a nonsmooth space dependency with* L^∞ *property. The essential parameters like diffusion coefficients and the dielectric permittivity are assumed to be positively bounded away from zero. Consequently the reference densities* $\boldsymbol{n}_*$ *depend nonsmoothly on* x*, too.*

There are several papers (see e.g. [GGH96, DeF06, GlG09] and papers cited there) on energy estimates for reaction-diffusion systems with reversible reactions (meaning that forward and reverse reaction are present). Here the free energy turns out to be a Lyapunov function and solutions converge to the unique steady state. Especially, the free energy decays monotonously and exponentially to its equilibrium value along solutions to the system. To prove this convergence, an estimate of the free energy by the dissipation rate is used. The investigations of Section 2 show that there is even an exact gradient structure under the stronger assumption of *detailed balance* (which happens to hold in most of the considered cases anyway). This gradient structure is based on the free energy $\mathcal{F}$ acting as the driving functional and the dual dissipation potential Ψ^*, which contains the diffusion part in terms of the Wasserstein-type term (see [Ott98, Ott01]) and the reaction term $\boldsymbol{H}$ introduced in [Mie11].

Similar results on convergence to equilibria as in [GGH96, GlG09] can be derived also for discretized electro-reaction-diffusion problems based on Voronoi finite-volume discretization in space and an implicit Euler scheme in time, see [Gli08b, Gli09b]. And the same properties remain true if (for the non-discretized situation) some model reduction under the assumption of partly fast kinetics are done, see [Gli09a]. A special case of uncharged species is investigated in [DeF06], where an explicite rate of convergence is obtained.

Remark 2.2 (Open systems) *There are different problems from device simulation (see e.g. [GaG90] for the van Roosbroeck equations, [Gli08a] for a spin-polarized drift-diffusion model, and [Gli10] for an electronic model for solar cells with energy resolved defect densities), where the underlying electro-reaction-diffusion system is not closed by homogeneous Neumann boundary conditions. There nontrivial Dirichlet boundary conditions on a part of the boundary of the device are prescribed and external sources may exist. In these situations at least the following assertions are obtained: If the boundary conditions and external source terms are compatible with thermodynamic equilibrium (cf.* (2.5)*), then the free energy along solutions decays monotonously to its equilibrium value. In the other case it may be increasing, but its growth can be estimated.*

3 Electro-reaction-diffusion systems with active interfaces

In this section we show that the abstract framework of gradient flows can be extended to include interfacial dynamics and still keeps thermodynamical correctness. Again heterostructures are taken into account. We study the following geometric setup, which easily can be generalized to several bulk parts and several interfaces with different material properties and different species and interactions inside these substructures.

We restrict ourselves to one bulk domain $\Omega \subset \mathbb{R}^N$ containing one active interface $\Gamma \subset \Omega$. We assume that Γ is orientable, such that we can consider limits from above and below. To make this rigorous we introduce two boundaries Γ^+ and Γ^- such that for any quantity u defined on Ω we denote by u^+ and u^- the limits from above and below, respectively. We then write shortly $u^\pm = u|_{\Gamma^\pm}$.

On the interface Γ we have I_Γ species denoted by $X_{\Gamma 1},\dots,X_{\Gamma I_\Gamma}$, we assign to them the density vector $\boldsymbol{n}_\Gamma \in \mathbb{R}^{I_\Gamma}$ for the carrier densities on Γ, which have a corresponding vector of charge numbers $\boldsymbol{q}_\Gamma$. The number and types of species may be different in the bulk and on the interface. Thus there is no direct way to compare the limits $\boldsymbol{n}^\pm$ and $\boldsymbol{n}_\Gamma$ on the interface. Similarly, we allow the thermodynamic driving forces $\boldsymbol{\eta}$ to have different limits $\boldsymbol{\eta}^+$, $\boldsymbol{\eta}^-$, and $\boldsymbol{\eta}_\Gamma$.

Again, we consider a closed system, meaning that for the species, living in the bulk, on $\partial\Omega$ no-flux boundary conditions are assumed. We take into account the following effects:

(a) volume reactions, where all involved species live in the bulk, namely

$$\sum_{i=1}^{I} \alpha_i^r X_i \underset{k_\mathrm{r}^r}{\overset{k_\mathrm{f}^r}{\rightleftharpoons}} \sum_{i=1}^{I} \beta_i^r X_i, \quad r=1,\dots,R,$$

as contained in the electro-reaction-diffusion systems studied in Section 2;

(b) transfer mechanisms and reactions between species on Γ^+, Γ^-, and Γ, namely

$$\sum_{i=1}^{I} \alpha_{i+}^r X_{i+} + \sum_{i=1}^{I} \alpha_{i-}^r X_{i-} + \sum_{i=1}^{I_\Gamma} \alpha_{\Gamma i}^r X_{\Gamma i} \underset{k_{\Gamma\mathrm{r}}^r}{\overset{k_{\Gamma\mathrm{f}}^r}{\rightleftharpoons}} \sum_{i=1}^{I} \beta_{i+}^r X_{i+} + \sum_{i=1}^{I} \beta_{i-}^r X_{i-} + \sum_{i=1}^{I_\Gamma} \beta_{\Gamma i}^r X_{\Gamma i},$$

$r=R+1,\dots,R+R_\Gamma$, where R_Γ is the number of different interfacial mechanisms and $\alpha_{i\pm}^r$, $\beta_{i\pm}^r$, $\alpha_{\Gamma i}^r$, and $\beta_{\Gamma i}^r$ are suitable stoichiometric coefficients.

Case (b) contains several different mechanisms, which are combined into one case for future notational convenience. To describe these mechanisms we introduce the integer-valued transfer matrices $B^\pm \in \mathbb{R}^{R_\Gamma\times I}$ and $C \in \mathbb{R}^{R_\Gamma\times I_\Gamma}$ resulting from the definition that the block matrix $(B^+,B^-,C) \in \mathbb{R}^{R_\Gamma\times(2I+I_\Gamma)}$ contains the rows

$$\Big((\alpha_{i+}^r-\beta_{i+}^r)_{i=1,\dots,I},(\alpha_{i-}^r-\beta_{i-}^r)_{i=1,\dots,I},(\alpha_{\Gamma i}^r-\beta_{\Gamma i}^r)_{i=I+1,\dots,I+I_\Gamma}\Big),$$

for $r=R+1,\dots,R+R_\Gamma$. Our assumption that all transfer processes of Case (b) are charge conserving is expressed by the condition

$$(B^+ + B^-)\boldsymbol{q} + C\boldsymbol{q}_\Gamma = 0.$$

To indicate the nature of the processes contained in Case (b) we now list a few possible simpler processes that are special subcases.

(b1) *Pure interfacial reaction* occurs for $r \in \{R{+}1,\dots,R{+}R_\Gamma\}$ if $B^+=0$ and $B^-=0$. In this case, the reactions in Γ are not coupled to the two boundaries Γ^+ and Γ^- of the bulk.

(b2) *Pure transmission* occurs if $C = 0$. In this case the species move from one side of the interface to the other without interacting with the species in the interface.

(b3) *Capture and escape from one side*, e.g. from Γ^+, occurs if $B^- = 0$. Then, the species can interact and move from Γ^+ to Γ or vice versa. Moreover, the species of Γ or Γ^+ can act as a catalyst for reaction in the other side.

Of course, in the general Case (b) the species on all three adjacent interfaces Γ, Γ^+, and Γ^- can interact.

In our further investigations we work with the vectors $\overline{\boldsymbol{n}} = (\boldsymbol{n}, \boldsymbol{n}_\Gamma) \in \mathbb{R}^{I+I_\Gamma}$ and $\overline{\boldsymbol{q}} = (\boldsymbol{q}, \boldsymbol{q}_\Gamma) \in \mathbb{Z}^{I+I_\Gamma}$. Moreover, we introduce the stoichiometric matrix $A \in \mathbb{Z}^{R\times I}$ having the rows

$$(\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r) \in \mathbb{Z}^I, \quad r = 1, \ldots, R.$$

We now define the block matrix $\overline{A}$ via

$$\overline{A} = \begin{pmatrix} A & 0 \\ B^+ + B^- & C \end{pmatrix} \in \mathbb{Z}^{(R+R_\Gamma)\times(I+I_\Gamma)}$$

and the enlarged stoichiometric subspace

$$\overline{\mathcal{S}} := \operatorname{range}\big(\overline{A}^\top\big) \subset \mathbb{R}^{I+I_\Gamma} \quad \text{giving} \quad \overline{\mathcal{S}}^\perp = \operatorname{kernel}\big(\overline{A}\big) \subset \mathbb{R}^{I+I_\Gamma}.$$

We can formulate the assumption of charge conservation of the interactions listed in Cases (a) and (b) by the property that $\overline{\boldsymbol{q}} \in \overline{\mathcal{S}}^\perp$. Moreover, all $\overline{\boldsymbol{p}} = (\boldsymbol{p}, \boldsymbol{p}_\Gamma) \in \overline{\mathcal{S}}^\perp$ generate invariant functionals

$$\mathcal{P}_{\overline{\boldsymbol{p}}}(\overline{\boldsymbol{n}}) = \int_{\Omega\setminus\Gamma} \boldsymbol{n}\cdot\boldsymbol{p}\,\mathrm{d}x + \int_\Gamma \boldsymbol{n}_\Gamma\cdot\boldsymbol{p}_\Gamma\,\mathrm{d}a. \tag{3.1}$$

Due to the definition of the matrices A, B^+, B^- and C we find

$$A\boldsymbol{p} = 0 \ \text{ and } \ (B^+ + B^-)\boldsymbol{p} + C\boldsymbol{p}_\Gamma = \boldsymbol{0} \quad \text{for all } \overline{\boldsymbol{p}} = (\boldsymbol{p}, \boldsymbol{p}_\Gamma) \in \overline{\mathcal{S}}^\perp. \tag{3.2}$$

We again want to work under the conditions of detailed balance, but now for the enlarged system including the interface interactions as well. Thus we impose the existence of positive reference densities $\overline{\boldsymbol{n}}_* = (\boldsymbol{n}_*, \boldsymbol{n}_{\Gamma*})$ with $\boldsymbol{n}_* : \Omega\setminus\Gamma \to \mathbb{R}^I$ and $\boldsymbol{n}_{\Gamma*} : \Gamma \to \mathbb{R}^{I_\Gamma}$ that are in *detailed balance*. This means that for all $\overline{\boldsymbol{n}} = (\boldsymbol{n}, \boldsymbol{n}_\Gamma)$ we have

$$k_\mathrm{f}^r(\boldsymbol{n})\boldsymbol{n}_*^{\boldsymbol{\alpha}^r} = k_\mathrm{r}^r(\boldsymbol{n})\boldsymbol{n}_*^{\boldsymbol{\beta}^r}, \qquad r = 1, \ldots, R, \tag{3.3a}$$

$$\begin{aligned} &k_{\Gamma\mathrm{f}}^r(\boldsymbol{n}^+, \boldsymbol{n}^-, \boldsymbol{n}_\Gamma)\big(\boldsymbol{n}_*^+\big)^{\boldsymbol{\alpha}_+^r}\big(\boldsymbol{n}_*^-\big)^{\boldsymbol{\alpha}_-^r}\big(\boldsymbol{n}_{\Gamma*}\big)^{\boldsymbol{\alpha}_\Gamma^r} \\ &\quad = k_{\Gamma\mathrm{r}}^r(\boldsymbol{n}^+, \boldsymbol{n}^-, \boldsymbol{n}_\Gamma)\big(\boldsymbol{n}_*^+\big)^{\boldsymbol{\beta}_+^r}\big(\boldsymbol{n}_*^-\big)^{\boldsymbol{\beta}_-^r}\big(\boldsymbol{n}_{\Gamma*}\big)^{\boldsymbol{\beta}_\Gamma^r}, \qquad r = R+1, \ldots, R+R_\Gamma, \end{aligned} \tag{3.3b}$$

where $\boldsymbol{n}_*^\pm$ are the corresponding one-sided limits of $\boldsymbol{n}_*$.

To see under what conditions this holds we first realize that the quotients

$$k_0^r := k_\mathrm{r}^r/k_\mathrm{f}^r \quad \text{and} \quad k_{\Gamma 0}^r := k_{\Gamma\mathrm{r}}^r/k_{\Gamma\mathrm{f}}^r$$

must be independent of $\overline{\boldsymbol{n}}$ (but may depend on $x \in \Omega \setminus \Gamma$ and $x \in \Gamma$, respectively, like $\overline{\boldsymbol{n}}_*$). Moreover, taking the logarithm of the relations (3.3) leads to the linear system

$$A \,\mathbf{log}\, \boldsymbol{n}_* = \mathbf{log}\, \boldsymbol{k}_0 := (\log k_0^r)_{r=1,\dots,R}, \quad x \in \Omega\backslash\Gamma, \tag{3.4a}$$

$$B^+ \mathbf{log}\, \boldsymbol{n}_*^+ + B^- \mathbf{log}\, \boldsymbol{n}_*^- + C\, \mathbf{log}\, \boldsymbol{n}_{\Gamma *} = \mathbf{log}\, \boldsymbol{k}_{\Gamma 0}, \quad x \in \Gamma, \tag{3.4b}$$

where $\mathbf{log}\, \boldsymbol{n}_*$ and $\mathbf{log}\, \boldsymbol{k}_{\Gamma 0}$ are the vectors $(\log n_{*i})_{i=1,\dots,I}$ and $(\log k_{\Gamma 0}^r)_{r=R+1,\dots,R+R_\Gamma}$, respectively. The condition in (3.4a) is exactly the condition (2.1) for the bulk, and we obviously have to assume that this system has at least one solution (however, there might be a whole family). The existence of the density $\overline{\boldsymbol{n}}_*$ now follows from generalized Wegscheider conditions by arguing as follows. For each point $x \in \Gamma$ we want to find densities $\widetilde{\boldsymbol{n}}^\pm$ and $\boldsymbol{n}_{\Gamma *}$ that have to satisfy the system

$$\mathbb{W} \begin{pmatrix} \mathbf{log}\, \widetilde{\boldsymbol{n}}^+ \\ \mathbf{log}\, \widetilde{\boldsymbol{n}}^- \\ \mathbf{log}\, \boldsymbol{n}_{\Gamma *} \end{pmatrix} = \begin{pmatrix} \mathbf{log}\, \boldsymbol{k}_0^+ \\ \mathbf{log}\, \boldsymbol{k}_0^- \\ \mathbf{log}\, \boldsymbol{k}_{\Gamma 0} \end{pmatrix}, \quad \text{where } \mathbb{W} = \begin{pmatrix} A & 0 & 0 \\ 0 & A & 0 \\ B^+ & B^- & C \end{pmatrix} \in \mathbb{R}^{(2R+R_\Gamma)\times(2I+I_\Gamma)} \tag{3.5}$$

and $k_0^{r\pm}$ denotes the limit of k_0^r on $\Gamma^\pm$. We call $\mathbb{W}$ the Wegscheider matrix of the system. We have $2R + R_\Gamma$ conditions to determine the $2I + I_\Gamma$ quantities $(\widetilde{\boldsymbol{n}}^+, \widetilde{\boldsymbol{n}}^-, \boldsymbol{n}_{\Gamma *})$. The Wegscheider conditions for the solvability of (3.5) now read $(\mathbf{log}\, \boldsymbol{k}_0^+, \mathbf{log}\, \boldsymbol{k}_0^-, \mathbf{log}\, \boldsymbol{k}_{\Gamma_0}) \in \mathrm{range}(\mathbb{W})$, which by Fredholm's alternative is equivalent to

$$\boldsymbol{y} \cdot (\mathbf{log}\, \boldsymbol{k}_0^+, \mathbf{log}\, \boldsymbol{k}_0^-, \mathbf{log}\, \boldsymbol{k}_{\Gamma 0})^\mathsf{T} = 0 \;\text{ for all } \boldsymbol{y} \in \mathrm{kernel}(\mathbb{W}^\mathsf{T}).$$

Finally, we can extend the solutions $\widetilde{\boldsymbol{n}}^\pm$ to $\boldsymbol{n}_* : \Omega\backslash\Gamma \to \mathbb{R}^I$ such that the one-sided limits satisfy $\boldsymbol{n}_*^\pm = \widetilde{\boldsymbol{n}}^\pm$.

The free energy for charged multi-species systems with active species on the interface Γ is given by the functional

$$\begin{aligned} \mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}}) &= \mathcal{F}_\Omega(\boldsymbol{n}) + \mathcal{F}_\Gamma(\boldsymbol{n}_\Gamma) \\ &= \int_{\Omega\backslash\Gamma} \Big\{ \frac{1}{2} \nabla\phi_{\overline{\boldsymbol{n}}} \cdot \varepsilon \nabla \phi_{\overline{\boldsymbol{n}}} + \sum_{i=1}^{I} n_i (\log \frac{n_i}{n_{*i}} - 1) \Big\} \,\mathrm{d}x + \int_\Gamma \sum_{i=1}^{I_\Gamma} n_{\Gamma i} (\log \frac{n_{\Gamma i}}{n_{\Gamma * i}} - 1) \,\mathrm{d}a. \end{aligned}$$

The part $\mathcal{F}_\Omega(\boldsymbol{n})$ is similar to the energy functional (2.4) for the electro-reaction-diffusion system without active interfaces studied in Section 2. But now the electrostatic potential $\phi_{\overline{\boldsymbol{n}}}$ is associated with the charge distributions in Ω and on Γ, namely

$$-\nabla \cdot (\varepsilon \nabla \phi) = d + \boldsymbol{q} \cdot \boldsymbol{n} + (d_\Gamma + \boldsymbol{q}_\Gamma \cdot \boldsymbol{n}_\Gamma)\delta_\Gamma \quad \text{in } \Omega,$$

and the same boundary conditions as in (2.2). Here δ_Γ denotes the surface measure on Γ such that in the sense of distributions $\int_\Omega v\, \gamma \delta_\Gamma \,\mathrm{d}x = \int_\Gamma \gamma v \,\mathrm{d}a$ for smooth v. For the invariant functionals $\mathcal{P}_{\overline{\boldsymbol{p}}}$ defined (3.1), $\overline{\boldsymbol{p}} \in \overline{\mathcal{S}}^{\perp}$, and the free energy functional we immediately obtain the derivatives

$$D\mathcal{P}_{\overline{\boldsymbol{p}}}(\overline{\boldsymbol{n}}) = \begin{pmatrix} \boldsymbol{p} \\ \boldsymbol{p}_\Gamma \end{pmatrix} \quad \text{and} \quad D\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}}) = \begin{pmatrix} \boldsymbol{\eta} \\ \boldsymbol{\eta}_\Gamma \end{pmatrix} =: \overline{\boldsymbol{\eta}}, \quad \text{where} \tag{3.6a}$$

$$\boldsymbol{\eta} = D_{\boldsymbol{n}}\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}}) = (\log \frac{n_i}{n_{*i}} + q_i\phi_{\overline{\boldsymbol{n}}})_{i=1,\dots,I} : \Omega\backslash\Gamma \to \mathbb{R}^I, \quad \text{and} \tag{3.6b}$$

$$\boldsymbol{\eta}_\Gamma = D_{\boldsymbol{n}_\Gamma}\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}}) = (\log \frac{n_{\Gamma i}}{n_{\Gamma * i}} + q_{\Gamma i}\phi_{\overline{\boldsymbol{n}}})_{i=1,\dots,I_\Gamma} : \Gamma \to \mathbb{R}^{I_\Gamma}. \tag{3.6c}$$

We give a proof of the formulas (3.6b) and (3.6c) within the proof of Theorem 3.1.

As before, $D\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}})$ defines the thermodynamic conjugate variables, which will act as driving forces. For the dual dissipation potential Ψ^*_{BI} we proceed analogously by introducing suitable integrals over the interface, namely

$$\Psi^*_{\mathrm{BI}}(\overline{\boldsymbol{n}}; \overline{\boldsymbol{\eta}}) = \Psi^*_{\Omega\backslash\Gamma}(\boldsymbol{n}; \boldsymbol{\eta}) + \Psi^*_\Gamma(\overline{\boldsymbol{n}}; \overline{\boldsymbol{\eta}}),$$

where $\Psi^*_{\Omega\backslash\Gamma}$ is as in (2.9), but integration has to be done over $\Omega \setminus \Gamma$, i.e. we do not assume continuity over the interface.

The dual interfacial dissipation potential Ψ^*_Γ will also consist of two parts, namely the interface diffusion part depending on the tangential gradients $\nabla_\Gamma \boldsymbol{\eta}_\Gamma$ and the transfer-reaction terms depending on $(\boldsymbol{\eta}^+, \boldsymbol{\eta}^-, \boldsymbol{\eta}_\Gamma)$. The latter case is associated with the transfers and reactions of Case (b) discussed above. The corresponding part in $\Psi^*_\Gamma(\overline{\boldsymbol{n}}; \overline{\boldsymbol{\eta}})$ only depends on the interfacial variables and the limits of the bulk variables from above and below at the interface, namely

$$\Psi^*_{\Gamma\,(\mathrm{b})}(\overline{\boldsymbol{n}}; \overline{\boldsymbol{\eta}}) = \int_\Gamma \psi^*_\Gamma(x, \boldsymbol{n}^+, \boldsymbol{n}^-, \boldsymbol{n}_\Gamma; \boldsymbol{\eta}^+, \boldsymbol{\eta}^-, \boldsymbol{\eta}_\Gamma)\,\mathrm{d}x,$$

where all functions are evaluated at $x \in \Gamma$. To give the general form for ψ^*_Γ and to relate it to the interface interactions defined in Case (b), we introduce the triples $\widehat{\boldsymbol{n}}$, $\widehat{\boldsymbol{\eta}} \in \mathbb{R}^{2I+I_\Gamma}$ and $\widehat{\boldsymbol{\alpha}}^r$, $\widehat{\boldsymbol{\beta}}^r \in \mathbb{N}_0^{2I+I_\Gamma}$ via

$$\widehat{\boldsymbol{n}} = (\boldsymbol{n}^+, \boldsymbol{n}^-, \boldsymbol{n}_\Gamma),\ \widehat{\boldsymbol{\eta}} = (\boldsymbol{\eta}^+, \boldsymbol{\eta}^-, \boldsymbol{\eta}_\Gamma),\ \widehat{\boldsymbol{\alpha}}^r = (\boldsymbol{\alpha}^r_+, \boldsymbol{\alpha}^r_-, \boldsymbol{\alpha}^r_\Gamma),\ \widehat{\boldsymbol{\beta}}^r = (\boldsymbol{\beta}^r_+, \boldsymbol{\beta}^r_-, \boldsymbol{\beta}^r_\Gamma). \tag{3.7}$$

The general form of the transfer and reaction density ψ^*_Γ is simply the quadratic form

$$\psi^*_\Gamma(x, \widehat{\boldsymbol{n}}; \widehat{\boldsymbol{\eta}}) = \frac{1}{2}\widehat{\boldsymbol{\eta}} \cdot \big(\boldsymbol{H}_\Gamma(x, \widehat{\boldsymbol{n}})\widehat{\boldsymbol{\eta}}\big),$$

where $\boldsymbol{H}_\Gamma(\widehat{\boldsymbol{n}}) \in \mathbb{R}^{(2I+I_\Gamma)\times(2I+I_\Gamma)}$ is symmetric and positive semi-definite. We continue to suppress the possible dependence on $x \in \Gamma$.

Moreover, $\boldsymbol{H}_\Gamma$ has to satisfy $\boldsymbol{H}_\Gamma(x, \widehat{\boldsymbol{n}})(\boldsymbol{p}, \boldsymbol{p}, \boldsymbol{p}_\Gamma) = 0$ for all $\overline{\boldsymbol{p}} = (\boldsymbol{p}, \boldsymbol{p}_\Gamma) \in \overline{\mathcal{S}}^{\perp}$ to keep the invariance of the functionals $\mathcal{P}_{\overline{\boldsymbol{p}}}$. In particular, the choice $\overline{\boldsymbol{p}} = (\boldsymbol{q}, \boldsymbol{q}_\Gamma)$ gives global charge conservation.

The reactions introduced in Case (b) can be realized by defining $\boldsymbol{H}_\Gamma$ in analogy to the bulk matrix $\boldsymbol{H}$ (cf. (2.6)), namely

$$\boldsymbol{H}_\Gamma(\widehat{\boldsymbol{n}}) := \sum_{r=R+1}^{R+R_\Gamma} k^r_{\Gamma\mathrm{f}}(\widehat{\boldsymbol{n}})\, \widehat{\boldsymbol{n}}_*^{\widehat{\boldsymbol{\alpha}}^r}\, \Lambda\Big(\frac{\widehat{\boldsymbol{n}}^{\widehat{\boldsymbol{\alpha}}^r}}{\widehat{\boldsymbol{n}}_*^{\widehat{\boldsymbol{\alpha}}^r}}, \frac{\widehat{\boldsymbol{n}}^{\widehat{\boldsymbol{\beta}}^r}}{\widehat{\boldsymbol{n}}_*^{\widehat{\boldsymbol{\beta}}^r}}\Big)\, (\widehat{\boldsymbol{\alpha}}^r{-}\widehat{\boldsymbol{\beta}}^r) \otimes (\widehat{\boldsymbol{\alpha}}^r{-}\widehat{\boldsymbol{\beta}}^r), \tag{3.8}$$

where $\widehat{\boldsymbol{n}}_*$ is the corresponding triple. In terms of the matrices B^+, B^-, and C introduced after Case (b) the matrix ψ^*_Γ can be written as

$$\psi^*_\Gamma(\widehat{\boldsymbol{n}}; \widehat{\boldsymbol{\eta}}) = \frac{1}{2}\Big((B^+, B^-, C)\widehat{\boldsymbol{\eta}}\Big) \cdot \boldsymbol{D}(\widehat{\boldsymbol{n}})\Big((B^+, B^-, C)\widehat{\boldsymbol{\eta}}\Big),$$

where $\boldsymbol{D} \in \mathbb{R}^{R_\Gamma \times R_\Gamma}$ is the diagonal matrix with the entries $k^r_{\Gamma\mathrm{f}}(\widehat{\boldsymbol{n}})\, \widehat{\boldsymbol{n}}_*^{\widehat{\boldsymbol{\alpha}}^r}\, \Lambda\Big(\frac{\widehat{\boldsymbol{n}}^{\widehat{\boldsymbol{\alpha}}^r}}{\widehat{\boldsymbol{n}}_*^{\widehat{\boldsymbol{\alpha}}^r}}, \frac{\widehat{\boldsymbol{n}}^{\widehat{\boldsymbol{\beta}}^r}}{\widehat{\boldsymbol{n}}_*^{\widehat{\boldsymbol{\beta}}^r}}\Big)$.

Using the detailed balance condition as well as the special form of the $\overline{\boldsymbol{\eta}}$ we find the desired relation

$$\widehat{\boldsymbol{R}}(\widehat{\boldsymbol{n}}) = -\boldsymbol{H}_\Gamma(\widehat{\boldsymbol{n}}) D\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}}) = -\sum_{r=R+1}^{R+R_\Gamma} \Big(k^r_{\Gamma\mathrm{f}}(\overline{\boldsymbol{n}})\widehat{\boldsymbol{n}}^{\widehat{\boldsymbol{\alpha}}^r} - k^r_{\Gamma\mathrm{r}}(\overline{\boldsymbol{n}})\widehat{\boldsymbol{n}}^{\widehat{\boldsymbol{\beta}}^r}\Big)\big(\widehat{\boldsymbol{\alpha}}^r{-}\widehat{\boldsymbol{\beta}}^r\big),$$

corresponding to the reactions assumed in Case (b). Interpreting this vector as the triple $\widehat{\boldsymbol{R}} = (\boldsymbol{J}^+, \boldsymbol{J}^-, \boldsymbol{R}_\Gamma)$, the component $\boldsymbol{R}_\Gamma$ contains the rates of the densities in the interface, while $\boldsymbol{J}^\pm$ corerspond to the fluxes leaving or entering the bulk via the boundary $\Gamma^\pm$.

As the total dual interfacial dissipation functional Ψ^*_Γ also contains mobility terms generating drift-diffusion processes of the interface species on the interface Γ, it has the form

$$\Psi^*_\Gamma(\overline{\boldsymbol{n}}; \overline{\boldsymbol{\eta}}) = \int_\Gamma \Big\{ \sum_{i=1}^{I_\Gamma} \frac{1}{2} \nabla_\Gamma \eta_{\Gamma i} \cdot \big(M_{\Gamma i}(\boldsymbol{n}_\Gamma)\nabla_\Gamma \eta_{\Gamma i}\big) + \psi^*_\Gamma(\widehat{\boldsymbol{n}}; \widehat{\boldsymbol{\eta}})\Big\}\, \mathrm{d}a, \tag{3.9}$$

where $\psi^*_\Gamma(\widehat{\boldsymbol{n}}; \widehat{\boldsymbol{\eta}})$ is as above. In the simplest case we have $M_{\Gamma i}(\boldsymbol{n}_\Gamma) = m_{\Gamma i} n_{\Gamma i}$ with a scalar diffusion coefficient $m_{\Gamma i}$, $i = 1, \ldots, I_\Gamma$. However, we may also generalize to cases allowing for cross-diffusion by choosing a fourth-order tensor $\boldsymbol{M}_\Gamma(\boldsymbol{n}_\Gamma)$ acting on the interfacial gradient $\nabla_\Gamma \boldsymbol{\eta}_\Gamma$.

We now come to the main result of this paper that establishes the form of the coupled bulk-interface model for $\overline{\boldsymbol{n}} = (\boldsymbol{n}, \boldsymbol{n}_\Gamma)$ generated by the gradient system for the bulk-interface potentials $\mathcal{F}_{\mathrm{BI}}$ and Ψ^*_{BI}.

Theorem 3.1 *Assume that $\mathcal{F}_{\mathrm{BI}}$ and Ψ^*_{BI} are given as above, then the gradient system*

$$\dot{\overline{\boldsymbol{n}}} = -D_{\overline{\boldsymbol{\eta}}} \Psi^*_{\mathrm{BI}}\big(\overline{\boldsymbol{n}}; D\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}})\big)$$

takes the form of the following system of coupled partial differential equations:

$$-\mathit{div}\big(\varepsilon\nabla\phi\big) = d + \boldsymbol{q}\cdot\boldsymbol{n} + (d_\Gamma + \boldsymbol{q}_\Gamma\cdot\boldsymbol{n}_\Gamma)\delta_\Gamma \qquad \text{in } \Omega, \tag{3.10a}$$

$$\dot{\boldsymbol{n}} = \mathit{div}\big(\boldsymbol{M}_{\mathit{bulk}}(\boldsymbol{n})\nabla\boldsymbol{\eta}\big) - \boldsymbol{H}_{\mathit{bulk}}(\boldsymbol{n})\boldsymbol{\eta} \qquad \text{in } \Omega\backslash\Gamma, \tag{3.10b}$$

$$\dot{\boldsymbol{n}}_\Gamma = \mathit{div}_\Gamma\big(\boldsymbol{M}_\Gamma(\boldsymbol{n}_\Gamma)\nabla_\Gamma\boldsymbol{\eta}_\Gamma\big) - P_\Gamma\boldsymbol{H}_\Gamma(\widehat{\boldsymbol{n}})\widehat{\boldsymbol{\eta}} \qquad \text{on } \Gamma, \tag{3.10c}$$

$$\big(\boldsymbol{M}_{\mathit{bulk}}(\boldsymbol{n})\nabla\boldsymbol{\eta}\big)\cdot\nu^+ = P_+\boldsymbol{H}_\Gamma(\widehat{\boldsymbol{n}})\widehat{\boldsymbol{\eta}} \qquad \text{on } \Gamma^+, \tag{3.10d}$$

$$\big(\boldsymbol{M}_{\mathit{bulk}}(\boldsymbol{n})\nabla\boldsymbol{\eta}\big)\cdot\nu^- = P_-\boldsymbol{H}_\Gamma(\widehat{\boldsymbol{n}})\widehat{\boldsymbol{\eta}} \qquad \text{on } \Gamma^-, \tag{3.10e}$$

where all usages of 'div' are to be understood in the weak form. Here $\boldsymbol{\eta} = \log \boldsymbol{n} - \log \boldsymbol{n}_* + \phi \boldsymbol{q}$, $\boldsymbol{\eta}_\Gamma = \log \boldsymbol{n}_\Gamma - \log \boldsymbol{n}_{\Gamma *} - \phi \boldsymbol{q}_\Gamma$, $\widehat{\boldsymbol{n}}$ *and* $\widehat{\boldsymbol{\eta}}$ *are defined in* (3.7), $\nu^\pm$ *are the outward normals pointing from* $\Gamma^\pm$ *towards* $\Gamma^\mp$*, and the projections* $P_\pm \in \mathbb{R}^{I\times(2I+I_\Gamma)}$ *and* $P_\Gamma \in \mathbb{R}^{I_\Gamma\times(2I+I_\Gamma)}$ *are given by*

$$P_+ := (I_{\mathbb{R}^I}, 0, 0), \quad P_- := (0, I_{\mathbb{R}^I}, 0), \quad P_\Gamma := (0, 0, I_{\mathbb{R}^{I_\Gamma}}).$$

In particular, sufficiently smooth solutions $\overline{\boldsymbol{n}}$ *of* (3.10) *satisfy the energy-dissipation relation*

$$\frac{d}{dt}\mathcal{F}_{\rm BI}(\overline{\boldsymbol{n}}(t)) = -2\Psi^*_{\rm BI}\Big(\overline{\boldsymbol{n}}(t); D\mathcal{F}_{\rm BI}\big(\overline{\boldsymbol{n}}(t)\big)\Big) \leq 0.$$

Remark 3.1 *The coupled electro-reaction-diffusion system with active interfaces stated in* (3.10) *consists of the following subsystems: The Poisson equation* (3.10a) *for the self-consistent calculation of the electrostatic potential* ϕ*, which contains at the right-hand side besides charge densities in the bulk also charges concentrated on the interface* Γ*. It is coupled with continuity equations on* $\Omega\setminus\Gamma$ *for the densities of the bulk species* (3.10b) *and continuity equations on the interface* Γ *for the species living on the interface only* (3.10c)*. Both types of continuity equations involve drift-diffusion fluxes and reaction terms defined in the bulk and on the interface, respectively. Finally, the equations* (3.10d) *and* (3.10e) *describe the normal fluxes of bulk species at the interface pointing from* $\Gamma^\pm$ *to* $\Gamma^\mp$ *in terms of rates of transfer mechanisms and reactions between species on* Γ^+, Γ^- *and* Γ.

Proof: We first establish the formulas for (3.6b) and (3.6c) for $\overline{\boldsymbol{\eta}} = D\mathcal{F}_{\rm BI}(\overline{\boldsymbol{n}})$. For this we calculate

$$\langle D\mathcal{F}_{\rm BI}(\overline{\boldsymbol{n}}), \boldsymbol{m})\rangle = \lim_{h\to 0}\frac{1}{h}\big(\mathcal{F}_{\rm BI}(\overline{\boldsymbol{n}}{+}h\overline{\boldsymbol{m}}){-}\mathcal{F}_{\rm BI}(\overline{\boldsymbol{n}})\big)$$

For this we use that $\phi_{\overline{\boldsymbol{n}}}$ depends affinely on $\overline{\boldsymbol{n}}$, such that

$$\widetilde{\phi}_{\overline{\boldsymbol{m}}} = \lim_{h\to 0}\frac{1}{h}\big(\phi_{\overline{\boldsymbol{n}}+h\overline{\boldsymbol{m}}}{-}\phi_{\overline{\boldsymbol{n}}}\big)$$

is the unique solution of the linear elliptic system

$$-\mathrm{div}\big(\varepsilon\nabla\phi\big) = \boldsymbol{q}\cdot\boldsymbol{m} + \boldsymbol{q}_\Gamma\cdot\boldsymbol{m}_\Gamma\,\delta_\Gamma, \quad \text{in } \Omega, \tag{3.11}$$

with the homogeneous version of the boundary conditions in (2.2).

Using the definition of $\mathcal{F}_{\rm BI}$ we now find

$$\langle D\mathcal{F}_{\rm BI}(\overline{\boldsymbol{n}}), \boldsymbol{m})\rangle = \int_{\Omega\setminus\Gamma}(\varepsilon\nabla\phi_{\overline{\boldsymbol{n}}})\cdot\nabla\widetilde{\phi}_{\overline{\boldsymbol{m}}} + (\log\boldsymbol{n}{-}\log\boldsymbol{n}_*)\cdot\boldsymbol{m}\,\mathrm{d}x$$
$$+\int_\Gamma(\log\boldsymbol{n}_\Gamma{-}\log\boldsymbol{n}_{\Gamma*})\cdot\boldsymbol{m}_\Gamma\,\mathrm{d}a.$$

Using (3.11) the first term on the right-hand side can be integrated by parts giving

$$\int_{\Omega\setminus\Gamma}(\varepsilon\nabla\phi_{\overline{\boldsymbol{n}}})\cdot\nabla\widetilde{\phi}_{\overline{\boldsymbol{m}}}\,\mathrm{d}x = -\int_{\Omega\setminus\Gamma}\phi_{\overline{\boldsymbol{n}}}\boldsymbol{q}\cdot\boldsymbol{m}\,\mathrm{d}x - \int_\Gamma\phi_{\overline{\boldsymbol{n}}}\boldsymbol{q}_\Gamma\cdot\boldsymbol{m}_\Gamma\,\mathrm{d}a.$$

Thus, (3.6b) and (3.6c) are established.

To derive system (3.10) we use a test function $\overline{\boldsymbol{\xi}}$ such that $\boldsymbol{\xi} : \Omega\backslash\Gamma \to \mathbb{R}^I$ and $\boldsymbol{\xi}_\Gamma : \Gamma \to \mathbb{R}^{I_\Gamma}$ are smooth and vanish on $\partial\Omega$ and $\partial\Gamma$, respectively. We note that this allows for $\boldsymbol{\xi}^+ \not\equiv \boldsymbol{\xi}^-$. Using the quadratic structure of Ψ^*_{BI} the gradient flow $\dot{\overline{\boldsymbol{n}}} = -D\Psi^*_{\mathrm{BI}}(\overline{\boldsymbol{n}}; D\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}}))$ implies

$$\begin{aligned}
\langle \dot{\overline{\boldsymbol{n}}}, \overline{\boldsymbol{\xi}}\rangle &= -\langle D\Psi^*_{\mathrm{BI}}(\overline{\boldsymbol{n}}; \overline{\boldsymbol{\eta}}), \overline{\boldsymbol{\xi}}\rangle \\
&= -\int_{\Omega\backslash\Gamma} (\boldsymbol{M}_{\mathrm{bulk}}\nabla\boldsymbol{\eta}) {:} \nabla\boldsymbol{\xi} + (\boldsymbol{H}_{\mathrm{bulk}}\boldsymbol{\eta})\cdot\boldsymbol{\xi}\,\mathrm{d}x - \int_\Gamma (\boldsymbol{M}_\Gamma\nabla_\Gamma\boldsymbol{\eta}_\Gamma) {:} \nabla_\Gamma\boldsymbol{\xi} + (\boldsymbol{H}_\Gamma\widehat{\boldsymbol{\eta}})\cdot\widehat{\boldsymbol{\xi}}\,\mathrm{d}a \\
&= \int_{\Omega\backslash\Gamma} \Big(\mathrm{div}\big(\boldsymbol{M}_{\mathrm{bulk}}\nabla\boldsymbol{\eta}\big) - \boldsymbol{H}_{\mathrm{bulk}}\boldsymbol{\eta}\Big)\cdot\boldsymbol{\xi}\,\mathrm{d}x + \int_\Gamma \Big(\mathrm{div}_\Gamma\big(\boldsymbol{M}_\Gamma\nabla_\Gamma\boldsymbol{\eta}_\Gamma\big) - P_\Gamma\boldsymbol{H}_\Gamma\widehat{\boldsymbol{\eta}}\Big)\cdot\boldsymbol{\xi}_\Gamma\,\mathrm{d}a \\
&\quad + \int_{\Gamma^+} \Big(\big(\boldsymbol{M}_{\mathrm{bulk}}\nabla\boldsymbol{\eta}\big)\nu^+ - P_+\boldsymbol{H}_\Gamma\widehat{\boldsymbol{\eta}}\Big)\cdot\boldsymbol{\xi}^+\mathrm{d}a + \int_{\Gamma^-} \Big(\big(\boldsymbol{M}_{\mathrm{bulk}}\nabla\boldsymbol{\eta}\big)\nu^- - P_+\boldsymbol{H}_\Gamma\widehat{\boldsymbol{\eta}}\Big)\cdot\boldsymbol{\xi}^-\mathrm{d}a.
\end{aligned}$$

Here we have used that integration by parts on $\Omega\backslash\Gamma$ gives different boundary terms on Γ^+ and Γ^- that have been sorted according to the three different test functions $\boldsymbol{\xi}_\Gamma = P_\Gamma\widehat{\boldsymbol{\xi}}$ and $\boldsymbol{\xi}^\pm = P_\pm\widehat{\boldsymbol{\xi}}$. Thus, (3.10) is established as well.

Moreover, choosing the test function $\overline{\boldsymbol{\xi}} = D\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}})$, i.e. $\boldsymbol{\xi} = D_{\boldsymbol{n}}\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}})$ and $\boldsymbol{\xi}_\Gamma = D_{\boldsymbol{n}_\Gamma}\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}})$ and using the first two lines of the last identity, the quadratic structure of Ψ^*_{BI} in (3.9) yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}}(t)) = \langle \dot{\overline{\boldsymbol{n}}}, D\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}})\rangle = -\langle D_{\overline{\boldsymbol{\eta}}}\Psi^*_{\mathrm{BI}}(\overline{\boldsymbol{n}}, \overline{\boldsymbol{\eta}}), D\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}})\rangle = -2\Psi^*_{\mathrm{BI}}(\overline{\boldsymbol{n}}, \overline{\boldsymbol{\eta}}) \leq 0,$$

which proves the decay of the free energy $\mathcal{F}_{\mathrm{BI}}$ along solutions $\overline{\boldsymbol{n}}$ of (3.10). □

Remark 3.2 *Since we again worked in heterostructures, let us summarize the space dependency of the physical parameters in this section. The bulk reaction constants* k^r_f, k^r_r, k^r_0, $r = 1, \ldots, R$, *the matrices* M_i, $i = 1, \ldots, I$, *and* ε, *and the bulk charge density* d *are allowed to depend nonsmoothly on* $x \in \Omega$ *with* $L^\infty(\Omega)$ *property. Moreover, the interface reaction constants* $k^r_{\Gamma f}$, $k^r_{\Gamma r}$, $k^r_{\Gamma 0}$, $r = R+1, \ldots, R+R_\Gamma$, *the left and right limits of the bulk reaction constants* $k^{r\pm}_f$, $k^{r\pm}_r$, $k^{r\pm}_0$, $r = 1, \ldots, R$, *and the quantities* $M_{\Gamma i}$ *and* d_Γ *are assumed to be* $L^\infty(\Gamma)$ *functions. Note that then the reference densities* $\boldsymbol{n}_*$, $\boldsymbol{n}_{\Gamma*}$ *and* $\boldsymbol{n}^\pm_*$ *are space dependent, too.*

4 Examples

In this section we study explicit applications of the above theory. In Subsection 4.1 a scalar diffusion equation coupled to an active interface is studied. In Subsection 4.2 we investigate reaction-diffusion systems of two bulk and two interfacial species, all uncharged. Finally, Subsection 4.3 discusses models for electrically charged species like electrons and holes. These models are relevant for modern solar cells, where the electronic properties of the interfaces contribute significantly to the efficiency of the cell, see [Gli10, Gli11] for more details on modeling of solar cells.

4.1 A single species diffusion model with active interface

We consider one uncharged species which lives in the bulk as X and at the interface Γ as X_Γ. Hence, the electrostatic potential ϕ can be neglected. We take into account diffusion in the bulk as well as on the interface. There is no bulk reaction but we consider the three transfer mechanisms of the species on Γ^+, Γ^-, and Γ

$$X_+ \underset{k^1_{\Gamma\mathrm{r}}}{\overset{k^1_{\Gamma\mathrm{f}}}{\rightleftharpoons}} X_\Gamma, \qquad X_- \underset{k^2_{\Gamma\mathrm{r}}}{\overset{k^2_{\Gamma\mathrm{f}}}{\rightleftharpoons}} X_\Gamma, \qquad X_+ \underset{k^3_{\Gamma\mathrm{r}}}{\overset{k^3_{\Gamma\mathrm{f}}}{\rightleftharpoons}} X_-. \tag{4.1}$$

Thus in our one species example we have $I = I_\Gamma = 1$, $R = 0$, and $R_\Gamma = 3$. Hence, A does not contain any row, and we obtain the matrices

$$\mathbb{W} = (B^+, B^-, C) = \begin{pmatrix} 1 & 0 & -1 \\ 0 & 1 & -1 \\ 1 & -1 & 0 \end{pmatrix} \quad \text{and} \quad \overline{A} = \begin{pmatrix} 1 & -1 \\ 1 & -1 \\ 0 & 0 \end{pmatrix}.$$

The enlarged stoichiometric subspace $\overline{\mathcal{S}}$ and its orthogonal complement have dimension one, especially $(1,1) \in \overline{\mathcal{S}}^\perp$, and thus the total mass of the species,

$$\mathcal{P}(\overline{\boldsymbol{n}}) = \int_{\Omega\setminus\Gamma} n \,\mathrm{d}x + \int_\Gamma n_\Gamma \,\mathrm{d}a, \tag{4.2}$$

is a conserved quantity. Using $\mathrm{kernel}(\mathbb{W}^\mathsf{T}) = \mathrm{span}(1,-1,-1)^\mathsf{T}$ the Wegscheider conditions on $k^r_{\Gamma 0} = k^r_{\Gamma\mathrm{r}}/k^r_{\Gamma\mathrm{f}}$ reduce to the single relation

$$k^1_{\Gamma 0} = k^2_{\Gamma 0} k^3_{\Gamma 0}.$$

Under this assumption, we can find positive reference densities $\overline{\boldsymbol{n}}_* = (n_*, n_{\Gamma *})$ such that (3.3) is fulfilled meaning that

$$k^1_{\Gamma\mathrm{f}} n^+_* = k^1_{\Gamma\mathrm{r}} n_{\Gamma *}, \quad k^2_{\Gamma\mathrm{f}} n^-_* = k^2_{\Gamma\mathrm{r}} n_{\Gamma *}, \quad k^3_{\Gamma\mathrm{f}} n^+_* = k^3_{\Gamma\mathrm{r}} n^-_*. \tag{4.3}$$

From the free energy functional

$$\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}}) = \int_{\Omega\setminus\Gamma} n\Big(\log\frac{n}{n_*} - 1\Big)\,\mathrm{d}x + \int_\Gamma n_\Gamma\Big(\log\frac{n_\Gamma}{n_{\Gamma *}} - 1\Big)\,\mathrm{d}a, \quad D\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}}) = \begin{pmatrix} \log\frac{n}{n_*} \\ \log\frac{n_\Gamma}{n_{\Gamma *}} \end{pmatrix} = \begin{pmatrix} \eta \\ \eta_\Gamma \end{pmatrix}$$

we obtain the driving forces for the evolution of the system, which represent the chemical potential in Ω and at Γ of the species. By means of the dual dissipation functional

$$\begin{aligned}\Psi^*_{\mathrm{BI}}(\overline{\boldsymbol{n}};\overline{\boldsymbol{\eta}}) = {}& \int_{\Omega\setminus\Gamma} \frac{m}{2} n|\nabla\eta|^2\,\mathrm{d}x + \int_\Gamma \Big\{\frac{m_\Gamma}{2} n_\Gamma |\nabla\eta_\Gamma|^2 + \frac{k^1_{\Gamma\mathrm{f}}}{2} n^+_* \Lambda\Big(\frac{n^+}{n^+_*}, \frac{n_\Gamma}{n_{\Gamma *}}\Big)(\eta^+ - \eta_\Gamma)^2\Big\}\,\mathrm{d}a \\ & + \int_\Gamma \Big\{\frac{k^2_{\Gamma\mathrm{f}}}{2} n^-_* \Lambda\Big(\frac{n^-}{n^-_*}, \frac{n_\Gamma}{n_{\Gamma *}}\Big)(\eta^- - \eta_\Gamma)^2 + \frac{k^3_{\Gamma\mathrm{f}}}{2} n^+_* \Lambda\Big(\frac{n^+}{n^+_*}, \frac{n^-}{n^-_*}\Big)(\eta^+ - \eta^-)^2\Big\}\,\mathrm{d}a\end{aligned}$$

we reconstruct the continuity equations in the bulk and at the interface

$$\begin{aligned} &\dot n - \operatorname{div}(m\, n\nabla\eta) = 0 && \text{in } \Omega\setminus\Gamma, \\ &\dot n_\Gamma - \operatorname{div}_\Gamma(m_\Gamma\, n_\Gamma \nabla_\Gamma \eta_\Gamma) = k^1_{\Gamma\mathrm{f}} n^+ - k^1_{\Gamma\mathrm{r}} n_\Gamma + k^2_{\Gamma\mathrm{f}} n^- - k^2_{\Gamma\mathrm{r}} n_\Gamma && \text{on } \Gamma, \end{aligned} \tag{4.4a}$$

and the conditions

$$\begin{aligned} -m\, n\nabla\eta\cdot\nu^+ &= k^1_{\Gamma\mathrm{f}} n^+ - k^1_{\Gamma\mathrm{r}} n_\Gamma + k^3_{\Gamma\mathrm{f}} n^+ - k^3_{\Gamma\mathrm{r}} n^- && \text{on } \Gamma^+, \\ -m\, n\nabla\eta\cdot\nu^- &= k^2_{\Gamma\mathrm{f}} n^- - k^2_{\Gamma\mathrm{r}} n_\Gamma - k^3_{\Gamma\mathrm{f}} n^+ + k^3_{\Gamma\mathrm{r}} n^- && \text{on } \Gamma^-. \end{aligned} \tag{4.4b}$$

Note that the right-hand sides in (4.4) are linear in $\overline{\boldsymbol{n}} = (n, n_\Gamma)$, which follows from the definition of Λ in (2.7). Have in mind that $k^j_{\Gamma\mathrm{r}}$ are obtained from the relations (4.3). Moreover, using the form of η and η_Γ we find $n\nabla\eta = \nabla n - n\nabla\log n_*$ and $n_\Gamma\nabla_\Gamma\eta_\Gamma = \nabla_\Gamma n_\Gamma - n_\Gamma\nabla\log n_{\Gamma*}$. Hence, we conclude that the whole system (4.4) is a linear system.

Finally, we remark that neglecting any of the above three transfer mechanisms leads to a similar linear system. The difference is that the corresponding Wegscheider matrix $\mathbb{W}$ then has full range and the Wegscheider conditions do not produce any restriction on the remaining quantities $k^j_{\Gamma 0}$. Hence, positive reference densities $\overline{\boldsymbol{n}}_*$ always exist. The total mass (4.2) remains a conserved quantity in that situation, too. The functionals $\mathcal{F}_{\mathrm{BI}}$ and Ψ^*_{BI} and the corresponding diffusion system is obtained from the above by simply dropping the corresponding terms.

4.2 Two reaction-diffusion systems

We consider a four-species model where all species are uncharged, so that the electrostatic potential ϕ can be neglected. We take into account two volume species X_1 and X_2 diffusing in the domain $\Omega\setminus\Gamma$ and undergoing the reaction $X_1 \rightleftharpoons X_2$ and two additional species $X_{\Gamma 1}$ and $X_{\Gamma 2}$ on Γ which diffuse there and undergo an interface reaction $X_{\Gamma 1} \rightleftharpoons X_{\Gamma 2}$, namely

$$X_1 \underset{k^1_{\mathrm{r}}}{\overset{k^1_{\mathrm{f}}}{\rightleftharpoons}} X_2, \qquad\qquad X_{\Gamma 1} \underset{k^2_{\Gamma\mathrm{r}}}{\overset{k^2_{\Gamma\mathrm{f}}}{\rightleftharpoons}} X_{\Gamma 2}. \tag{4.5}$$

In the first case we only consider one transfer mechanism between Γ^+, Γ^-, and Γ. One particle of species X_1 from the upper boundary Γ^+ and one particle X_2 from Γ^- can combine to two particles $X_{\Gamma 2}$, which is called the 'capture into the interface'. The reverse mechanism is called the 'escape from the interface'. Symbolically this interaction is written as

$$X_{1+} + X_{2-} \underset{k^3_{\Gamma\mathrm{r}}}{\overset{k^3_{\Gamma\mathrm{f}}}{\rightleftharpoons}} 2\, X_{\Gamma 2}.$$

In this example we have $I = I_\Gamma = 2$, $R = 1$, $R_\Gamma = 2$ and the matrices A, $B^\pm$, C and $\overline{A}$ from Section 3 have the form $A = (1\ \ -1) \in \mathbb{R}^{1\times 2}$,

$$B^+ = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}, \quad B^- = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}, \quad C = \begin{pmatrix} 1 & -1 \\ 0 & -2 \end{pmatrix}, \quad \overline{A} = \begin{pmatrix} 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 \\ 1 & 1 & 0 & -2 \end{pmatrix}.$$

The stoichiometric subspace is

$$\overline{\mathcal{S}} = \operatorname{span}\big\{(1,-1,0,0),\ (0,0,1,-1),\ (1,1,0,-2)\big\}, \quad \overline{\mathcal{S}}^\perp = \operatorname{span}\big\{(1,1,1,1)\big\}.$$

Therefore

$$\mathcal{P}(\overline{\boldsymbol{n}}) = \int_{\Omega\setminus\Gamma} (n_1 + n_2)\,\mathrm{d}x + \int_\Gamma (n_{\Gamma 1} + n_{\Gamma 2})\,\mathrm{d}a$$

generates the space of conserved quantities.

For simplicity, we assume the reaction rate constants not depending on the state. We discuss the generalized Wegscheider conditions guaranteeing the existence of positive reference densities $\overline{\boldsymbol{n}}_* = (\boldsymbol{n}_*, \boldsymbol{n}_{\Gamma *})$ with (3.4). The condition for the bulk (3.4a) does not produce any restriction. Now we have to calculate $(\widetilde{\boldsymbol{n}}^+, \widetilde{\boldsymbol{n}}^-, \boldsymbol{n}_{\Gamma *})\colon \Gamma \to \mathbb{R}^6$ fulfilling (3.5) (and finally we extend $\widetilde{\boldsymbol{n}}^\pm$ to $\boldsymbol{n}_*\colon \Omega\setminus\Gamma \to \mathbb{R}^2$ with $\boldsymbol{n}_*^\pm = \widetilde{\boldsymbol{n}}^\pm$). For the solvability of (3.5) for our model with respect to $(\log \widetilde{n}_1^+, \log \widetilde{n}_2^+, \log \widetilde{n}_1^-, \log \widetilde{n}_2^-, \log n_{\Gamma *1}, \log n_{\Gamma *2})$ we have to ensure that the right-hand side $(\log k_0^{1+}, \log k_0^{1-}, \log k_{\Gamma 0}^2, \log k_{\Gamma 0}^3)$ lies in the range of the Wegscheider matrix

$$\mathbb{W} = \begin{pmatrix} A & 0 & 0 \\ 0 & A & 0 \\ B^+ & B^- & C \end{pmatrix} = \left(\begin{array}{cc|cc|cc} 1 & -1 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 1 & -1 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 1 & -1 \\ 1 & 0 & 0 & 1 & 0 & -2 \end{array}\right) \in \mathbb{R}^{4\times 6}.$$

Since $\mathbb{W}$ has full range, the Wegscheider condition is always satisfied, and we find positive $\boldsymbol{n}_*, \boldsymbol{n}_{\Gamma *}$ such that

$$k_\mathrm{f}^1 n_{*1} = k_\mathrm{r}^1 n_{*2}, \quad k_{\Gamma\mathrm{f}}^2 n_{\Gamma *1} = k_{\Gamma\mathrm{r}}^2 n_{\Gamma *2}, \quad k_{\Gamma\mathrm{f}}^3 n_{*1}^+ n_{*2}^- = k_{\Gamma\mathrm{r}}^3 {n_{\Gamma *2}}^2.$$

From the free energy functional

$$\mathcal{F}_\mathrm{BI}(\overline{\boldsymbol{n}}) = \int_{\Omega\setminus\Gamma} \sum_{i=1}^2 n_i(\log \frac{n_i}{n_{*i}} - 1)\,\mathrm{d}x + \int_\Gamma \sum_{i=1}^2 n_{\Gamma i}(\log \frac{n_{\Gamma i}}{n_{\Gamma * i}} - 1)\,\mathrm{d}a \tag{4.6}$$

we obtain the driving forces for the evolution, namely the chemical potentials of the species

$$D\mathcal{F}_\mathrm{BI}(\overline{\boldsymbol{n}}) = \begin{pmatrix} (\log \frac{n_i}{n_{*i}})_{i=1,2} \\ (\log \frac{n_{\Gamma i}}{n_{\Gamma * i}})_{i=1,2} \end{pmatrix} = \begin{pmatrix} \boldsymbol{\eta} \\ \boldsymbol{\eta}_\Gamma \end{pmatrix}.$$

By means of the dual dissipation potential

$$
\begin{aligned}
\Psi^*_{\mathrm{BI}}(\overline{\boldsymbol{n}};\overline{\boldsymbol{\eta}}) = &\int_\Omega \Big\{ \sum_{i=1}^2 \frac{m_i}{2} n_i |\nabla \eta_i|^2 + \frac{k_{\mathrm{f}}^1}{2} n_{*1} \Lambda\Big(\frac{n_1}{n_{*1}}, \frac{n_2}{n_{*2}}\Big)(\eta_1-\eta_2)^2 \Big\} \,\mathrm{d}x \\
&+ \int_\Gamma \Big\{ \sum_{i=1}^2 \frac{m_{\Gamma i}}{2} n_{\Gamma i} |\nabla \eta_{\Gamma i}|^2 + \frac{k_{\Gamma\mathrm{f}}^2}{2} n_{\Gamma *1} \Lambda\Big(\frac{n_{\Gamma 1}}{n_{\Gamma *1}}, \frac{n_{\Gamma 2}}{n_{\Gamma *2}}\Big)(\eta_{\Gamma 1}-\eta_{\Gamma 2})^2 \\
&\qquad + \frac{k_{\Gamma\mathrm{r}}^3}{2} n_{\Gamma *2}^2 \Lambda\Big(\frac{n_1^+ n_2^-}{n_{*1}^+ n_{*2}^-}, \frac{{n_{\Gamma 2}}^2}{{n_{\Gamma *2}}^2}\Big)(\eta_1^+ + \eta_2^- - 2\eta_{\Gamma 2})^2 \Big\} \,\mathrm{d}a
\end{aligned}
\tag{4.7}
$$

we reconstruct the corresponding reaction diffusion system. It consists of the continuity equations in $\Omega \setminus \Gamma$ and Γ, respectively,

$$
\left.
\begin{aligned}
\dot n_1 - \operatorname{div}(m_1 n_1 \nabla \eta_1) &= -k_{\mathrm{f}}^1 n_1 + k_{\mathrm{r}}^1 n_2 \\
\dot n_2 - \operatorname{div}(m_2 n_2 \nabla \eta_2) &= k_{\mathrm{f}}^1 n_1 - k_{\mathrm{r}}^1 n_2
\end{aligned}
\right\} \text{in } \Omega\setminus\Gamma,
$$

$$
\left.
\begin{aligned}
\dot n_{\Gamma 1} - \operatorname{div}_\Gamma(m_{\Gamma 1} n_{\Gamma 1} \nabla_\Gamma \eta_{\Gamma 1}) &= -k_{\Gamma\mathrm{f}}^2 n_{\Gamma 1} + k_{\Gamma\mathrm{r}}^2 n_{\Gamma 2} \\
\dot n_{\Gamma 2} - \operatorname{div}_\Gamma(m_{\Gamma 2} n_{\Gamma 2} \nabla_\Gamma \eta_{\Gamma 2}) &= k_{\Gamma\mathrm{f}}^2 n_{\Gamma 1} - k_{\Gamma\mathrm{r}}^2 n_{\Gamma 2} + 2(k_{\Gamma\mathrm{f}}^3 n_1^+ n_2^- - k_{\Gamma\mathrm{r}}^3 {n_{\Gamma 2}}^2)
\end{aligned}
\right\} \text{on } \Gamma,
\tag{4.8a}
$$

and the interface conditions

$$
\left.
\begin{aligned}
-m_1 n_1 \nabla \eta_1 \cdot \nu^+ &= k_{\Gamma\mathrm{f}}^3 n_1^+ n_2^- - k_{\Gamma\mathrm{r}}^3 {n_{\Gamma 2}}^2 \\
-m_2 n_2 \nabla \eta_2 \cdot \nu^+ &= 0
\end{aligned}
\right\} \text{ on } \Gamma^+,
$$

$$
\left.
\begin{aligned}
-m_1 n_1 \nabla \eta_1 \cdot \nu^- &= 0 \\
-m_2 n_2 \nabla \eta_2 \cdot \nu^- &= k_{\Gamma\mathrm{f}}^3 n_1^+ n_2^- - k_{\Gamma\mathrm{r}}^3 {n_{\Gamma 2}}^2
\end{aligned}
\right\} \text{ on } \Gamma^-.
\tag{4.8b}
$$

Here we again wrote the reaction and transfer terms explicitly after exploiting the definition of Λ in (2.7) and the detailed balance conditions associated with $k^r_{\mathrm{f,r}}$, $k^r_{\Gamma\,\mathrm{f,r}}$, $\boldsymbol{n}_*$, and $\boldsymbol{n}_{\Gamma *}$. Note that the right-hand sides now contain quadratic terms. As in the previous example we may insert the definition of the driving forces $\boldsymbol{\eta}$ and $\boldsymbol{\eta}_\Gamma$ to see that the fluxes $n_i \nabla \eta_i = \nabla n_i - n_i \nabla \log n_{i*}$ and $n_{\Gamma i} \nabla_\Gamma \eta_{\Gamma i} = \nabla_\Gamma n_{\Gamma i} - n_{\Gamma i} \nabla_\Gamma \log n_{\Gamma i *}$ are linear.

We now extend the above system by adding a second transfer mechanism at the interface Γ. More preciesely, we keep the two bulk reactions (4.5) and consider the two transfer mechanisms

$$
X_{1+} + X_{2-} \underset{k_{\Gamma\mathrm{r}}^3}{\overset{k_{\Gamma\mathrm{f}}^3}{\rightleftharpoons}} 2\,X_{\Gamma 2}, \qquad X_{1-} + X_{2+} \underset{k_{\Gamma\mathrm{r}}^4}{\overset{k_{\Gamma\mathrm{f}}^4}{\rightleftharpoons}} 2\,X_{\Gamma 2}.
$$

We have $I = I_\Gamma = 2$, $R = 1$, $R_\Gamma = 3$, and the matrices

$$\mathbb{W} = \begin{pmatrix} A & 0 & 0 \\ 0 & A & 0 \\ B^+ & B^- & C \end{pmatrix} = \left(\begin{array}{cc|cc|cc} 1 & -1 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 1 & -1 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 1 & -1 \\ 1 & 0 & 0 & 1 & 0 & -2 \\ 0 & 1 & 1 & 0 & 0 & -2 \end{array}\right), \quad \overline{A} = \begin{pmatrix} 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 \\ 1 & 1 & 0 & -2 \\ 1 & 1 & 0 & -2 \end{pmatrix}.$$

The stoichiometric subspace $\overline{\mathcal{S}} = \mathrm{range}(\overline{A}^\mathsf{T})$ and $\overline{\mathcal{S}}^\perp = \mathrm{kernel}\overline{A} = \mathrm{span}\big\{(1,1,1,1)^\mathsf{T}\big\}$ remain as before, giving the conserved quantity

$$\mathcal{P}(\overline{\boldsymbol{n}}) = \int_{\Omega\setminus\Gamma} (n_1 + n_2)\,\mathrm{d}x + \int_\Gamma (n_{\Gamma 1} + n_{\Gamma 2})\,\mathrm{d}a.$$

The Wegscheider condition is obtained from $\mathrm{kernel}(\mathbb{W}^\mathsf{T}) = \mathrm{span}(1,-1,0,-1,1)^\mathsf{T}$ and reduces to

$$\log k_0^{1+} - \log k_0^{1-} - \log k_{\Gamma 0}^3 + \log k_{\Gamma 0}^4 = 0.$$

Thus, if the condition

$$k_0^{1+} k_{\Gamma 0}^4 = k_0^{1-} k_{\Gamma 0}^3$$

is fulfilled, system (3.5) can be solved, and we find positive $\boldsymbol{n}_*, \boldsymbol{n}_{\Gamma *}$ such that

$$\begin{aligned} k_\mathrm{f}^1 n_{*1} &= k_\mathrm{r}^1 n_{*2}, & k_{\Gamma\mathrm{f}}^2 n_{\Gamma *1} &= k_{\Gamma\mathrm{r}}^2 n_{\Gamma *2}, \\ k_{\Gamma\mathrm{f}}^3 n_{*1}^+ n_{*2}^- &= k_{\Gamma\mathrm{r}}^3 {n_{\Gamma *2}}^2, & k_{\Gamma\mathrm{f}}^4 n_{*1}^- n_{*2}^+ &= k_{\Gamma\mathrm{r}}^4 {n_{\Gamma *2}}^2. \end{aligned}$$

The free energy $\mathcal{F}_\mathrm{BI}$ remains as in (4.6), whereas the dual dissipation potential Ψ_BI^* is obtained from (4.7) by adding the new interaction term

$$+ \int_\Gamma \Big\{ \frac{k_{\Gamma\mathrm{r}}^4}{2} {n_{\Gamma *2}}^2 \Lambda\Big(\frac{n_1^-}{n_{*1}^-}\frac{n_2^+}{n_{*2}^+}, \frac{{n_{\Gamma 2}}^2}{{n_{\Gamma *2}}^2} \Big) (\eta_1^- + \eta_2^+ - 2\eta_{\Gamma 2})^2 \Big\}\,\mathrm{d}a.$$

The reaction-diffusion system arising from the gradient system $\dot{\overline{\boldsymbol{n}}} = -D_{\boldsymbol{\eta}} \Psi_\mathrm{BI}^*(\overline{n}; D\mathcal{F}_\mathrm{BI}(\overline{\boldsymbol{n}}))$ has exactly the form of (4.8) except for the following three equations containing the additional terms involving the constant k_Γ^4:

$$\begin{aligned} \dot n_{\Gamma 2} - \mathrm{div}_\Gamma\,(m_{\Gamma 2} n_{\Gamma 2} \nabla_\Gamma \eta_{\Gamma 2}) &= k_{\Gamma\mathrm{f}}^2 n_{\Gamma 1} - k_{\Gamma\mathrm{r}}^2 n_{\Gamma 2} + 2(k_{\Gamma\mathrm{f}}^3 n_1^+ n_2^- - k_{\Gamma\mathrm{r}}^3 {n_{\Gamma 2}}^2) \\ &\quad + 2(k_{\Gamma\mathrm{f}}^4 n_1^- n_2^+ - k_{\Gamma\mathrm{r}}^4 {n_{\Gamma 2}}^2) && \text{on } \Gamma\,, \\ -m_2 n_2 \nabla\eta_2 \cdot \nu^+ &= k_{\Gamma\mathrm{f}}^4 n_1^- n_2^+ - k_{\Gamma\mathrm{r}}^4 {n_{\Gamma 2}}^2 && \text{on } \Gamma^+, \\ -m_1 n_1 \nabla\eta_1 \cdot \nu^- &= k_{\Gamma\mathrm{f}}^4 n_1^- n_2^+ - k_{\Gamma\mathrm{r}}^4 {n_{\Gamma 2}}^2 && \text{on } \Gamma^-. \end{aligned}$$

4.3 A model for electronic properties of solar cells

As in all semiconductor models, in solar cells the charge of the species is of great importance. Since the problem has to be considered in heterostructures, the reference quantities $\boldsymbol{n}_*$ and $\boldsymbol{n}_{\Gamma *}$ in general depend in a nonsmooth way on the space variable. We consider here a reduced model where only one type of traps (defects), namely acceptor-like traps living on the interface Γ are taken into account. More general electronic models for solar cells contain different kinds of traps, also being distributed in the bulk and they involve energy-resolved defect densities. (See e.g. [SLH10, Sect. 4] for the model equations, [Gli10] for the analysis of corresponding bulk models with traps also only in the bulk, and [Gli11] for the analysis of a model with bulk-interface coupling).

In the bulk we have as mobile species electrons $X_1 = \mathrm{e}^-$ and holes $X_2 = h^+$ with charge numbers $q_1 = -q_2 = -1$. There occurs the recombination and generation reaction $e^- + p^+ \rightleftharpoons \emptyset$, viz.

$$X_1 + X_2 \quad \underset{k_{\mathrm{r}}^1}{\overset{k_{\mathrm{f}}^1}{\rightleftharpoons}} \quad \emptyset.$$

The desired reaction in solar cells is the generation $\emptyset \rightharpoondown e^- + p^+$, which is initiated by photons, whereas the recombination $e^- + p^+ \rightharpoonup \emptyset$ leads to losses.

At the interface Γ we consider immobile acceptor-like traps $X_{\Gamma 1}$ (with negative charge $q_{\Gamma 1} = -1$) and $X_{\Gamma 2}$ (neutral, $q_{\Gamma 2} = 0$). Moreover, there take place ionization reactions for the traps using bulk electrons and bulk holes from the left and right side, viz.

$$X_{1+}{+}X_{\Gamma 2} \underset{k_{\Gamma\mathrm{r}}^2}{\overset{k_{\Gamma\mathrm{f}}^2}{\rightleftharpoons}} X_{\Gamma 1}, \quad X_{1-}{+}X_{\Gamma 2} \underset{k_{\Gamma\mathrm{r}}^3}{\overset{k_{\Gamma\mathrm{f}}^3}{\rightleftharpoons}} X_{\Gamma 1}, \quad X_{2+}{+}X_{\Gamma 1} \underset{k_{\Gamma\mathrm{r}}^4}{\overset{k_{\Gamma\mathrm{f}}^4}{\rightleftharpoons}} X_{\Gamma 2}, \quad X_{2-}{+}X_{\Gamma 1} \underset{k_{\Gamma\mathrm{r}}^6}{\overset{k_{\Gamma\mathrm{f}}^5}{\rightleftharpoons}} X_{\Gamma 2}.$$

We also allow for the process of thermionic emission of electrons and holes through the interface, viz.

$$X_{1+} \underset{k_{\Gamma\mathrm{r}}^6}{\overset{k_{\Gamma\mathrm{f}}^6}{\rightleftharpoons}} X_{1-} \quad \text{and} \quad X_{2+} \underset{k_{\Gamma\mathrm{r}}^7}{\overset{k_{\Gamma\mathrm{f}}^7}{\rightleftharpoons}} X_{2-}\ .$$

Thus, for this model we have $I = I_\Gamma = 2$, $R = 1$, $R_\Gamma = 6$, and the matrices A, $B^\pm$, C, $\mathbb{W}$, and $\overline{A}$ from Section 3 read

$$\mathbb{W} = \begin{pmatrix} A & 0 & 0 \\ 0 & A & 0 \\ B^+ & B^- & C \end{pmatrix} = \left(\begin{array}{cc|cc|cc} 1 & 1 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 1 & 1 & 0 & 0 \\ \hline 1 & 0 & 0 & 0 & -1 & 1 \\ 0 & 0 & 1 & 0 & -1 & 1 \\ 0 & 1 & 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 1 & 1 & -1 \\ 1 & 0 & -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & -1 & 0 & 0 \end{array}\right), \quad \overline{A} = \begin{pmatrix} 1 & 1 & 0 & 0 \\ 1 & 0 & -1 & 1 \\ 1 & 0 & -1 & 1 \\ 0 & 1 & 1 & -1 \\ 0 & 1 & 1 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

Simple calculations show that $\dim \overline{\mathcal{S}} = \dim \overline{\mathcal{S}}^{\perp} = 2$ and that the total charge and the total amount of traps

$$\mathcal{Q}(\overline{\boldsymbol{n}}) = \int_{\Omega\setminus\Gamma} \boldsymbol{n}\cdot\boldsymbol{q}\,\mathrm{d}x + \int_{\Gamma} \boldsymbol{n}_{\Gamma}\cdot\boldsymbol{q}_{\Gamma}\,\mathrm{d}a, \qquad \mathcal{P}(\overline{\boldsymbol{n}}) = \int_{\Gamma}(n_{\Gamma 1}+n_{\Gamma 2})\,\mathrm{d}a$$

span the whole space of conserved quantities. Since the traps are assumed to be immobile, the density $n_{\Gamma 1}+n_{\Gamma 2}$ is conserved locally, too.

To use the gradient structure $\dot{\overline{\boldsymbol{n}}} = -D_{\boldsymbol{\eta}}\Psi^{*}_{\mathrm{BI}}(\overline{\boldsymbol{n}}, D\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}}))$ we need to be able to choose suitable positive bulk and interface reference densities $\boldsymbol{n}_*$ and $\boldsymbol{n}_{\Gamma*}$ fulfilling (3.4). This is guaranteed by the following arguments. Equation (3.4a) can be solved without additional assumptions. Next, we have to solve (3.5) for the present model. The linear equation for

$$(\log\widetilde{n}_1^{+}, \log\widetilde{n}_2^{+}, \log\widetilde{n}_1^{-}, \log\widetilde{n}_2^{-}, \log n_{\Gamma*1}, \log n_{\Gamma*2})$$

can be solved with the right-hand side

$$(\log k_0^{1+}, \log k_0^{1-}, \log k_{\Gamma 0}^{2}, \log k_{\Gamma 0}^{3}, \log k_{\Gamma 0}^{4}, \log k_{\Gamma 0}^{5}, \log k_{\Gamma 0}^{6}, \log k_{\Gamma 0}^{7}),$$

if it lies in range($\mathbb{W}$). From kernel($\mathbb{W}^{\mathsf{T}}$) =

$$= \mathrm{span}\big\{(-1,0,0,1,1,0,1,0)^{\mathsf{T}}, (1,0,-1,0,-1,0,0,0)^{\mathsf{T}}, (0,1,0,-1,0,-1,0,0)^{\mathsf{T}}\big\}$$

and Fredholm's alternative we find three Wegscheider conditions. Hence, (3.5) can be solved if and only if the reactions constants satisfy

$$k_{\Gamma 0}^{3}k_{\Gamma 0}^{4}k_{\Gamma 0}^{6} = k_0^{1+}, \quad k_{\Gamma 0}^{2}k_{\Gamma 0}^{4} = k_0^{1+}, \quad k_{\Gamma 0}^{3}k_{\Gamma 0}^{5} = k_0^{1-} \quad \text{on } \Gamma.$$

Now the electro-reaction-diffusion system for the solar cell with bulk-interface coupling is obtained as gradient flow in the setting of Section 3 with the free energy functional

$$\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}}) = \int_{\Omega\setminus\Gamma}\Big\{\frac{1}{2}\nabla\phi_{\overline{\boldsymbol{n}}}\cdot(\varepsilon\nabla\phi_{\overline{\boldsymbol{n}}}) + \sum_{i=1}^{2} n_i(\log\frac{n_i}{n_{*i}}-1)\Big\}\,\mathrm{d}x + \int_{\Gamma}\sum_{i=1}^{2} n_{\Gamma i}(\log\frac{n_{\Gamma i}}{n_{\Gamma * i}}-1)\,\mathrm{d}a,$$

where $\boldsymbol{n}_*$ and $\boldsymbol{n}_{\Gamma*}$ are some positive bulk and interface reference densities, respectively, fulfilling (3.4) and $\phi_{\overline{\boldsymbol{n}}}$ is the unique solution to the Poisson equation

$$-\nabla\cdot(\varepsilon\nabla\phi) = d - n_1 + n_2 + (d_\Gamma - n_{\Gamma 1})\delta_\Gamma \text{ in } \Omega \tag{4.9a}$$

with the boundary conditions in (2.2). Here d and d_Γ denote fixed given charge densities (dopings) in the bulk and on the interface, respectively. Let $\boldsymbol{n}_*^{\pm}$ be the (possibly different) limits of the bulk quantity $\boldsymbol{n}_*$ on both sides of the interface. Then, the dual dissipation functional takes the form

$$
\begin{aligned}
&\Psi^*_{\mathrm{BI}}(\overline{\boldsymbol{n}};\overline{\boldsymbol{\eta}}) \ = \\
&\int_{\Omega\setminus\Gamma}\Big\{\sum_{i=1}^{2}\frac{m_i}{2}n_i|\nabla\eta_i|^2+\frac{k_{\mathrm{f}}^1}{2}n_{*1}n_{*2}\Lambda\big(\tfrac{n_1n_2}{n_{*1}n_{*2}},1\big)(\eta_1{+}\eta_2)^2\Big\}\,\mathrm{d}x\,+\\
&\int_{\Gamma}\Big\{\frac{k_{\Gamma\mathrm{f}}^2}{2}n_{*1}^+n_{\Gamma*2}\Lambda\big(\tfrac{n_1^+n_{\Gamma2}}{n_{*1}^+n_{\Gamma*2}},\tfrac{n_{\Gamma1}}{n_{\Gamma*1}}\big)(\eta_1^+{+}\eta_{\Gamma2}{-}\eta_{\Gamma1})^2+\frac{k_{\Gamma\mathrm{f}}^3}{2}n_{*1}^-n_{\Gamma*2}\Lambda\big(\tfrac{n_1^-n_{\Gamma2}}{n_{*1}^-n_{\Gamma*2}},\tfrac{n_{\Gamma1}}{n_{\Gamma*1}}\big)(\eta_1^-{+}\eta_{\Gamma2}{-}\eta_{\Gamma1})^2\\
&\quad+\frac{k_{\Gamma\mathrm{f}}^4}{2}n_{*2}^+n_{\Gamma*1}\Lambda\big(\tfrac{n_2^+n_{\Gamma1}}{n_{*2}^+n_{\Gamma*1}},\tfrac{n_{\Gamma2}}{n_{\Gamma*2}}\big)(\eta_2^+{+}\eta_{\Gamma1}{-}\eta_{\Gamma2})^2+\frac{k_{\Gamma\mathrm{f}}^5}{2}n_{*2}^-n_{\Gamma*1}\Lambda\big(\tfrac{n_2^-n_{\Gamma1}}{n_{*2}^-n_{\Gamma*1}},\tfrac{n_{\Gamma2}}{n_{\Gamma*2}}\big)(\eta_2^-{+}\eta_{\Gamma1}{-}\eta_{\Gamma2})^2\\
&\quad+\frac{k_{\Gamma\mathrm{f}}^6}{2}n_{*1}^+\Lambda\big(\tfrac{n_1^+}{n_{*1}^+},\tfrac{n_1^-}{n_{*1}^-}\big)(\eta_1^+{-}\eta_1^-)^2+\frac{k_{\Gamma\mathrm{f}}^7}{2}n_{*2}^+\Lambda\big(\tfrac{n_2^+}{n_{*2}^+},\tfrac{n_2^-}{n_{*2}^-}\big)(\eta_2^+{-}\eta_2^-)^2\Big\}\,\mathrm{d}a.
\end{aligned}
$$

Recall that the traps $X_{\Gamma1}$ and $X_{\Gamma2}$ in the interface are assumed to be immobile, hence the terms $\nabla_\Gamma\eta_{\Gamma i}$ do not occur. Together with the thermodynamic conjugate variables

$$
\begin{pmatrix}\boldsymbol{\eta}\\ \boldsymbol{\eta}_\Gamma\end{pmatrix}=D\mathcal{F}_{\mathrm{BI}}(\overline{\boldsymbol{n}})=\begin{pmatrix}(\log\frac{n_i}{n_{*i}}+q_i\phi_{\overline{\boldsymbol{n}}})_{i=1,2}\\ (\log\frac{n_{\Gamma i}}{n_{\Gamma*i}}+q_{\Gamma i}\phi_{\overline{\boldsymbol{n}}})_{i=1,2}\end{pmatrix}, \tag{4.9b}
$$

where $\phi_{\overline{\boldsymbol{n}}}$ solves the Poisson equation (4.9a) from the generalized gradient flow formulation (1.1) we obtain the following coupled system

$$
\begin{aligned}
&\left.\begin{aligned}\dot n_1+\operatorname{div}j_{n_1}&=-k_{\mathrm{f}}^1n_1n_2+k_{\mathrm{r}}^1\\ \dot n_2+\operatorname{div}j_{n_2}&=-k_{\mathrm{f}}^1n_1n_2+k_{\mathrm{r}}^1\end{aligned}\right\}\ \text{in }\Omega\setminus\Gamma,\\
&\left.\begin{aligned}\dot n_{\Gamma1}=\ &k_{\Gamma\mathrm{f}}^2n_1^+n_{\Gamma2}-k_{\Gamma\mathrm{r}}^2n_{\Gamma1}+k_{\Gamma\mathrm{f}}^3n_1^-n_{\Gamma2}-k_{\Gamma\mathrm{r}}^3n_{\Gamma1}\\ &-k_{\Gamma\mathrm{f}}^4n_2^+n_{\Gamma1}+k_{\Gamma\mathrm{r}}^4n_{\Gamma2}-k_{\Gamma\mathrm{f}}^5n_2^-n_{\Gamma1}+k_{\Gamma\mathrm{r}}^5n_{\Gamma2},\\ \dot n_{\Gamma2}=\ &-k_{\Gamma\mathrm{f}}^2n_1^+n_{\Gamma2}+k_{\Gamma\mathrm{r}}^2n_{\Gamma1}-k_{\Gamma\mathrm{f}}^3n_1^-n_{\Gamma2}+k_{\Gamma\mathrm{r}}^3n_{\Gamma1}\\ &+k_{\Gamma\mathrm{f}}^4n_2^+n_{\Gamma1}-k_{\Gamma\mathrm{r}}^4n_{\Gamma2}+k_{\Gamma\mathrm{f}}^5n_2^-n_{\Gamma1}-k_{\Gamma\mathrm{r}}^5n_{\Gamma2},\end{aligned}\right\}\ \text{on }\Gamma,
\end{aligned} \tag{4.9c}
$$

and the extra conditions at the interface

$$
\begin{aligned}
&\left.\begin{aligned}j_{n_1}\cdot\nu^+&=k_{\Gamma\mathrm{f}}^2n_1^+n_{\Gamma2}-k_{\Gamma\mathrm{r}}^2n_{\Gamma1}+k_{\Gamma\mathrm{f}}^6n_1^+-k_{\Gamma\mathrm{r}}^6n_1^-\\ j_{n_2}\cdot\nu^+&=k_{\Gamma\mathrm{f}}^4n_2^+n_{\Gamma1}-k_{\Gamma\mathrm{r}}^4n_{\Gamma2}+k_{\Gamma\mathrm{f}}^7n_2^+-k_{\Gamma\mathrm{r}}^7n_2^-\end{aligned}\right\}\ \text{on }\Gamma^+,\\
&\left.\begin{aligned}j_{n_1}\cdot\nu^-&=k_{\Gamma\mathrm{f}}^3n_1^-n_{\Gamma2}-k_{\Gamma\mathrm{r}}^3n_{\Gamma1}-k_{\Gamma\mathrm{f}}^6n_1^++k_{\Gamma\mathrm{r}}^6n_1^-\\ j_{n_2}\cdot\nu^-&=k_{\Gamma\mathrm{f}}^5n_2^-n_{\Gamma1}-k_{\Gamma\mathrm{r}}^5n_{\Gamma2}-k_{\Gamma\mathrm{f}}^7n_2^++k_{\Gamma\mathrm{r}}^7n_2^-\end{aligned}\right\}\ \text{on }\Gamma^-,
\end{aligned} \tag{4.9d}
$$

where the flux terms (currents) are given by $j_{n_i}=-m_in_i\nabla\eta_i$, $i=1,2$, with $\boldsymbol{\eta}$ from (4.9b). The system is then closed by recalling that $\phi_{\overline{\boldsymbol{n}}}$ is determined by the Poisson equation (4.9a).

Remark 4.1 (Modeling freedom) *In the present case, the advantage of the gradient structure is obvious, as it is otherwise not easy to determine the thermodynamic correctness of such complicated coupled systems. In a naïve modeling of the reactions in* (4.9c) *and* (4.9d)*, one would have to choose 36 coefficients for the right hand sides. In contrast, it is clear from the form of* $\mathcal{F}_{\mathrm{BI}}$ *and* Ψ^*_{BI} *that we can choose only the seven forward reaction rates* k^1_f, $k^2_{\Gamma f}, ..., k^7_{\Gamma f}$ *and the four reference densities* n_{*1}, n_{*2}, $n_{\Gamma *1}$, $n_{\Gamma *3}$. *Of course, this is equivalent to the approach using reactions of mass-action type and invoking the Wegscheider conditions: the seven reverse reaction rates* k^1_r, $k^2_{\Gamma r}, ..., k^7_{\Gamma r}$ *are determined by three Wegscheider conditions and the choices of the four reference densities.*

In similarity to the results for the corresponding bulk model in [Gli10], the analytical properties of the model proposed in [SLH10, Sect. 4] and given in its simplest form by (4.9) is studied in [Gli11].

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