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Energy estimates for continuous and discretized electro-reaction-diffusion systems

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Abstract

We consider electro-reaction-diffusion systems consisting of continuity equations for a finite number of species coupled with a Poisson equation. We take into account heterostructures, anisotropic materials and rather general statistic relations.

We investigate thermodynamic equilibria and prove for solutions to the evolution system the monotone and exponential decay of the free energy to its equilibrium value. Here the essential idea is an estimate of the free energy by the dissipation rate which is proved indirectly.

The same properties are shown for an implicit time discretized version of the problem. Moreover, we provide a space discretized scheme for the electro-reaction-diffusion system which is dissipative (the free energy decays monotonously). On a fixed grid we use for each species different Voronoi boxes which are defined with respect to the anisotropy matrix occurring in the flux term of this species.

1 Model equations, notation, and assumptions

Let $\Omega \subset \mathbb{R}^d$ be a bounded domain, $\Gamma := \partial\Omega$. We consider m electrically charged species X_ν with charge numbers q_ν and initial densities U_ν. These species underly drift-diffusion processes and take part in chemical reactions. We assume that the free energy of the system is a sum of a chemical and an (electrostatic) interaction part, where the chemical part is a sum of 1-species free energies. This leads to state equations giving the relation between the densities u_ν of the species X_ν and the corresponding chemical potentials v_ν of type

$$u_\nu = \overline{u}_\nu g_\nu(v_\nu - \overline{v}_\nu), \quad \nu = 1, \dots, m. \tag{1}$$

The functions $\overline{u}_\nu$ and $\overline{v}_\nu$ are known reference densities and reference potentials, respectively. The fact that the reference values may depend on the spatial position expresses the possible heterogeneity of the system under consideration. The functions g_ν reflect the underlying statistics. In the case of Boltzmann statistics each g_ν is the exponential function. Our assumptions with respect to g_ν are such that all cases of practical interest are included, in particular the Fermi–Dirac statistics. Moreover, in the case where the chemical part of the free energy is a sum of 1-species free energies the inverse Hessian matrix is diagonal with its ν-th component $\overline{u}_\nu g_\nu'(v_\nu - \overline{v}_\nu)$.

Let v_0 denote the electrostatic potential. To describe the fluxes j_ν of the species X_ν we need the electrochemical potential $\zeta_\nu := v_\nu + q_\nu v_0$. According to [2, 8, 19], we assume that the driving force of the flux is the antigradient of the electrochemical potential and that the flux is proportional the inverse Hessian. In the simplest case with Boltzmann statistics and no anisotropies of the material j_ν is proportional to $-u_\nu \nabla\zeta_\nu$. In this paper we suppose that

$$j_\nu = -\overline{u}_\nu g_\nu'(v_\nu - \overline{v}_\nu)\mathbf{S}_\nu(\cdot)\nabla\zeta_\nu, \; \nu = 1, \dots, m, \tag{2}$$

where $\mathbf{S}_\nu$ is a pointwise given $d \times d$ matrix function which prescribes the anisotropy of the material

$$\mathbf{S}_\nu(x) = Q_\nu^T(x)\mathrm{diag}\big(\mu_\nu^1(x), \dots, \mu_\nu^d(x)\big)Q_\nu(x). \tag{3}$$

The d-dimensional orthogonal matrices Q_ν and Q_ν^T have to be introduced since in general the crystallographic axes and the orientation of the modeled heterostructure do not coincide. Then the anisotropic mobility matrix in diagonal form $\mathrm{diag}(\mu^1,\dots,\mu^d)$ can be applied and Q_ν^T serves for the back transformation (see e.g. [15, 16, 17]). Moreover the structure of the flux terms reflects the fact that the inverse Hessian of the part of the ν-th species in the free energy has to be a factor in the flux term (see [2, 8, 19]). In the sequel δ denotes an appropriate strictly positive constant, and the subscript $+$ indicates the standard positive cone in a space. For the anisotropic mobility matrix we suppose that $\mu_\nu^k \in L_+^\infty(\Omega)$, $\text{ess inf}_\Omega \mu_\nu^k \geq \delta$, $k = 1,\dots d$, $\nu = 1,\dots,m$. Especially let us remark that under these assumptions the matrix $\mathbf{S}_\nu$ a.e. on Ω is symmetric and positive definite, what is needed in many estimates.

To describe chemical reactions we assume that $\mathcal{R} \subset \mathbb{Z}_+^m \times \mathbb{Z}_+^m$ is a finite subset. A pair $(\alpha,\beta) \in \mathcal{R}$ represents the vectors of stoichiometric coefficients of reversible reactions, usually written in the following form:

$$\alpha_1 X_1 + \dots + \alpha_m X_m \rightleftharpoons \beta_1 X_1 + \dots + \beta_m X_m.$$

We assume that the net rate of this pair of reactions is of the form $k_{\alpha\beta}(a^\alpha - a^\beta)$, where $k_{\alpha\beta}$ is a reaction coefficient, $a_\nu := \exp(\zeta_\nu)$ is the electrochemical activity of X_ν, and $a^\alpha := \prod_{\nu=1}^m a_\nu^{\alpha_\nu}$. In this model we replaced the concentrations by activities. This is necessary for the model to be in accordance with the Second Law of Thermodynamics (cf. Othmer [18]). The net production rate of species X_ν corresponding to the reaction rates for all reactions taking place is

$$R_\nu := \sum_{(\alpha,\beta)\in\mathcal{R}} k_{\alpha\beta}(a^\alpha - a^\beta)(\beta_\nu - \alpha_\nu). \tag{4}$$

The continuity equation for the concentrations taking into account reaction, diffusion, and drift processes can be written as follows:

$$\begin{gathered}\frac{\partial u_\nu}{\partial t} + \nabla\cdot j_\nu = R_\nu \text{ in } \mathbb{R}_+\times\Omega, \quad n\cdot j_\nu = 0 \text{ on } \mathbb{R}_+\times\Gamma,\\ u_\nu(0) = U_\nu \text{ in } \Omega, \quad \nu = 1,\dots,m.\end{gathered} \tag{5}$$

The Poisson equation satisfied by the electrostatic potential has the form

$$-\nabla\cdot(\mathbf{S}_\varepsilon \nabla v_0) = f + \sum_{\nu=1}^m q_\nu u_\nu \quad \text{in } \mathbb{R}_+\times\Omega, \quad n\cdot(\mathbf{S}_\varepsilon v_0) + \tau v_0 = f^\Gamma \quad \text{on } \mathbb{R}_+\times\Gamma, \tag{6}$$

where $\mathbf{S}_\varepsilon$ is the dielectric permittivity matrix

$$\mathbf{S}_\varepsilon(x) = Q_\varepsilon^T(x)\mathrm{diag}(\varepsilon^1(x),\dots,\varepsilon^d(x))Q_\varepsilon(x) \tag{7}$$

with a (diagonal) dielectric permittivity matrix $\mathrm{diag}(\varepsilon^1(x),\dots,\varepsilon^d(x))$ and some orthogonal matrix Q_ε. Supposing that $\varepsilon^k \in L_+^\infty(\Omega)$, $\text{ess inf}_\Omega \varepsilon^k \geq \delta$, $k = 1,\dots,d$, the matrix $\mathbf{S}_\varepsilon$ a.e. on Ω becomes symmetric and positive definite, too. In some cases where a unified notation gives advantages (see Section 4) we write $\mathbf{S}_0$, Q_0, μ_0^k instead of $\mathbf{S}_\varepsilon$, Q_ε, ε^k.

Now we collect assumptions which we suppose to be fulfilled in the paper.

(A1) Ω is a bounded Lipschitzian domain in $\mathbb{R}^2$, $\Gamma = \partial\Omega$;

(A2) $g_\nu \in C^1(\mathbb{R}),\ \overline{u}_\nu \in L^\infty_+(\Omega),\ \overline{u}_\nu \geq \delta,\ \overline{v}_\nu \in L^\infty(\Omega),\ \nu = 1,\dots,m,$

$\lim_{y\to\infty} \frac{1}{y} g_\nu(y) = +\infty,\ 0 < \delta \min\{1, g_\nu(y)\} \leq g'_\nu(y) \leq \delta^{-1} g_\nu(y),$

$\delta \min\{1, \exp(y)\} \leq g_\nu(y) \leq \delta^{-1}\exp(y),\ \nu = 1,\dots,m,\ y \in \mathbb{R};$

(A3) $\mu^k_\nu \in L^\infty_+(\Omega),\ \text{ess inf}_\Omega \mu^k_\nu \geq \delta,\ k = 1,2,\ \nu = 1,\dots,m;$

(A4) $\mathcal{R} \subset \mathbb{Z}^m_+ \times \mathbb{Z}^m_+$ finite subset, $k_{\alpha\beta} \in L^\infty_+(\Omega),\ \int_\Omega k_{\alpha\beta}\,\mathrm{d}x > 0$ for $(\alpha,\beta) \in \mathcal{R}$;

(A5) $U_\nu \in L^\infty_+(\Omega),\ q_\nu \in \mathbb{Z},\ \nu = 1,\dots,m;$

(A6) $\varepsilon^k \in L^\infty_+(\Omega),\ \text{ess inf}_\Omega \varepsilon^k \geq \delta,\ k = 1,2,\ \tau \in L^\infty_+(\Gamma),\ \int_\Gamma \tau \mathrm{d}\Gamma > 0,$

$f \in L^\infty(\Omega),\ f^\Gamma \in L^\infty(\Gamma).$

Existence results for special realizations of the electro-reaction-diffusion system (5), (6) (without anisotropies, ansatzes for the fluxes not related to the inverse Hessian of the free energy, special statistics, restrictions concerning the reaction terms) in the sense of weak solutions can be found in [6, 7, 12]. In this paper we are interested in energy estimates for the continuous and discrete time and space version of (5), (6). Again, for the continuous problem in special situations we have already obtained results (see [10] and [11] (Boltzmann statistics only)).

To give a weak formulation of the equations (5), (6) we introduce the following spaces:

$$V := H^1(\Omega;\mathbb{R}^{m+1}),\ W := \{v \in V :\ \exp(v_\nu) \in L^\infty(\Omega),\ \nu = 1,\dots,m\}, \tag{8}$$

and the stoichiometric subspaces

$$\mathcal{S} := \operatorname{span}\{\alpha - \beta : (\alpha,\beta) \in \mathcal{R}\},\ \ \mathcal{S}^\perp := \text{orthogonal complement of } \mathcal{S} \text{ in } \mathbb{R}^m. \tag{9}$$

In addition to (A1) – (A6) we assume that we are given $U \in V^*$ such that

(A7) $U = \Big(\sum_{\nu=1}^m q_\nu U_\nu, U_1,\dots,U_m\Big),\ \sum_{\nu=1}^m \lambda_\nu \langle U_\nu, 1\rangle > 0$ if $\lambda = (\lambda_1,\dots,\lambda_m) \in \mathcal{S}^\perp_+ \backslash \{0\}.$

V^* denotes the space dual to V, and 1 means the constant function on Ω taking the value 1. Note that (A7) with respect to U is satisfied if $U_\nu \geq 0$, $U_\nu \neq 0$, $\nu = 1,\dots,m$. The element U plays the role of an initial value for the vector function $u := (u_0,\dots,u_m)$, where

$$u_0 = \sum_{\nu=1}^m q_\nu u_\nu \tag{10}$$

is the charge density.

Next we define operators $A : W \to V^*$, and $E : V \to V^*$ as follows:

$$\begin{aligned}\langle Av, \widehat{v}\rangle \;&:=\; \int_\Omega \sum_{\nu=1}^m e_\nu'(\cdot, v_\nu)\, \mathbf{S}_\nu \nabla\zeta_\nu \cdot \nabla\widehat{\zeta_\nu}\, \mathrm{d}x \\ &\quad + \int_\Omega \sum_{(\alpha,\beta)\in\mathcal{R}} k_{\alpha\beta}(a^\alpha - a^\beta)(\alpha-\beta)\cdot\widehat{\zeta}\,\mathrm{d}x, \quad v \in W,\, \widehat{v}\in V,\end{aligned} \tag{11}$$

where $a := (\exp(\zeta_1), \dots, \exp(\zeta_m))$, $\zeta_\nu = v_\nu + q_\nu v_0$, $\widehat{\zeta_\nu} = \widehat{v}_\nu + q_\nu \widehat{v}_0$, $\nu = 1, \dots, m$,

$$\langle E_0 v_0, \widehat{v}_0\rangle := \int_\Omega \big(\mathbf{S}_\varepsilon \nabla v_0 \cdot \nabla \widehat{v}_0 - f\widehat{v}_0\big)\mathrm{d}x + \int_\Gamma \big(\tau v_0 - f^\Gamma\big)\widehat{v}_0\,\mathrm{d}\Gamma, \quad v_0,\, \widehat{v}_0 \in H^1(\Omega), \tag{12}$$

$$Ev := (E_0 v_0, e_1(\cdot, v_1), \dots, e_m(\cdot, v_m)), \quad v \in V, \tag{13}$$

where

$$e_\nu(x,y) := \overline{u}_\nu(x) g_\nu(y - \overline{v}_\nu(x)) \text{ for } x \in \overline{\Omega},\, y\in\mathbb{R},\; \nu = 1,\dots,m, \tag{14}$$

and $e_\nu'(\cdot, y)$ means the derivative with respect to the second argument. Using (A6) we obtain that $E_0 : H^1(\Omega) \to H^1(\Omega)^*$ is strongly monotone, i.e., there exists $\gamma > 0$ such that

$$\langle E_0 v_0 - E_0 w_0, v_0 - w_0\rangle \ge \gamma \|v_0 - w_0\|_{H^1}^2 \;\text{ for } v_0, w_0 \in H^1(\Omega). \tag{15}$$

Now we write the transient problem (5), (6) with (1), (2) and (4) more precisely as follows:

$$\begin{aligned}&u'(t) + Av(t) = 0,\; u(t) = Ev(t) \text{ f.a.a. } t \in \mathbb{R}_+,\; u(0) = U,\\ &u \in H^1_{\mathrm{loc}}(\mathbb{R}_+; V^*),\; v \in L^2_{\mathrm{loc}}(\mathbb{R}_+; V) \cap L^\infty_{\mathrm{loc}}(\mathbb{R}_+; W).\end{aligned} \tag{16}$$

For $v \in V$ the value

$$D(v) := \int_\Omega \sum_{\nu=1}^m e_\nu'(\cdot, v_\nu)\, \mathbf{S}_\nu\, \nabla\zeta_\nu \cdot \nabla\zeta_\nu\,\mathrm{d}x + \int_\Omega \sum_{(\alpha,\beta)\in\mathcal{R}} k_{\alpha\beta}(e^{\zeta\cdot\alpha} - e^{\zeta\cdot\beta})(\alpha-\beta)\cdot\zeta\mathrm{d}x \tag{17}$$

is called the dissipation rate associated to v. The reason for this terminology is the following. If (u, v) is a solution to the initial value problem (16) then

$$D(v(t)) = \langle Av(t), v(t)\rangle = -\langle u'(t), v(t)\rangle,$$

and in thermodynamics this expression is the dissipation rate of the process governed by (16) at time t.

To define the free energy of a state of the system under consideration we first introduce a functional $G : V \to \mathbb{R}$ as follows:

$$\begin{aligned}G(v) := &\int_\Omega \big(\frac{1}{2}\mathbf{S}_\varepsilon \nabla v_0 \cdot \nabla v_0 - f v_0\big)\,\mathrm{d}x + \int_\Gamma \big(\frac{\tau}{2} v_0^2 - f^\Gamma v_0\big)\,\mathrm{d}\Gamma\\ &+ \int_\Omega \sum_{\nu=1}^m \int_0^{v_\nu} e_\nu(\cdot, y)\,\mathrm{d}y\,\mathrm{d}x.\end{aligned} \tag{18}$$

The functional G is continuous, strictly convex and Gâteaux differentiable, hence subdifferentiable and $\partial G = E$. The conjugate of the functional G will be denoted by F,

$$F(u) := \sup_{v\in V} \big\{ \langle u, v\rangle - G(v) \big\}. \tag{19}$$

F is proper, lower semicontinuous and convex. Moreover, it holds $u = Ev = \partial G(v)$ if and only if $v \in \partial F(u)$. For $u \in V^*$ the value $F(u)$ is to be interpreted as the free energy of the state u. We are interested in a relation between the free energy and the dissipation rate. To describe this relation we need some information about stationary solutions to (16).

2 Thermodynamic equilibria

We define

$$\mathcal{U} := \Big\{ u \in V^* : \; u_0 = \sum_{\nu=1}^m q_\nu u_\nu, \; (\langle u_1, 1\rangle, \dots, \langle u_m, 1\rangle) \in \mathcal{S} \Big\}. \tag{20}$$

If (u, v) is a solution to (16) then $u(t) - U \in \mathcal{U}$ for every $t > 0$. Therefore, if $u^* := \lim_{t\to\infty} u(t)$ exists, then we have necessarily $u^* \in U + \mathcal{U}$. The set $\mathcal{U}^\perp := \{ v \in V : \langle u, v\rangle = 0$ for every $u \in \mathcal{U}\}$ can be characterized as follows:

$$\mathcal{U}^\perp = \Big\{ v \in V : \; \nabla\zeta = 0, \, \zeta_\nu = v_\nu + q_\nu v_0, \, \zeta = (\zeta_1, \dots, \zeta_m) \in \mathcal{S}^\perp \Big\}.$$

We cite some earlier result (cf. [10, Lemma 3.3]). There it is proved without the matrix function $\mathbf{S}_\varepsilon$. But due to (A6) an estimate

$$\gamma \|v_0\|^2_{H^1} \le \int_\Omega \mathbf{S}_\varepsilon \nabla v_0 \cdot \nabla v_0 \,\mathrm{d}x + \int_\Gamma \tau v_0^2 \,\mathrm{d}\Gamma \le \widetilde{\gamma} \|v_0\|^2_{H^1}, \quad v_0 \in H^1(\Omega) \tag{21}$$

holds, and the techniques can be applied in this case, too.

Lemma 2.1 *The functional $G_0 := G + I_{\mathcal{U}^\perp} - U$ is proper, convex, and lower semicontinuous. It satisfies* $\lim_{\|v\|_V\to\infty} G_0(v) = +\infty$.

Here $I_{U^\perp}$ denotes the indicator functional of $\mathcal{U}^\perp$, vanishing on $\mathcal{U}^\perp$ and taking the value $+\infty$ on $V\backslash\mathcal{U}^\perp$.

Theorem 2.1 *There exists a unique $v^* \in W$ such that $Av^* = 0$ and $u^* := Ev^* \in U + \mathcal{U}$. It holds $\nabla\zeta^* = 0$ and $\zeta^* \in \mathcal{S}^\perp$.*

Proof. 1. By Lemma 2.1 there exists a v^* such that $G_0(v^*)$ is the minimal value of G_0. Then $0 \in \partial G_0(v^*)$. We have

$$\partial G_0 = E + \partial I_{\mathcal{U}^\perp} - U, \;\; \partial I_{\mathcal{U}^\perp}(v) = \mathcal{U} \text{ for } v \in \mathcal{U}^\perp. \tag{22}$$

Since $v^* \in \mathcal{U}^\perp$ we find $0 = Ev^* + u - U$ for some $u \in \mathcal{U}$. Therefore,

$$E_0 v_0^* = U_0 - u_0 = \sum_{\nu=1}^m q_\nu (U_\nu - u_\nu) = \sum_{\nu=1}^m q_\nu e_\nu(\cdot, v_\nu^*) = \sum_{\nu=1}^m q_\nu e_\nu(\cdot, \zeta_\nu^* - q_\nu v_0^*),$$

where $\zeta_\nu^* = v_\nu^* + q_\nu v_0^*$. Using Grögers boundedness result [13], (A2) and (A6) we find that $v_0^* \in L^\infty(\Omega)$. This implies that $v_\nu^* = \zeta_\nu^* - q_\nu v_0^* \in L^\infty(\Omega),\ \nu = 1, \dots, m$.
2. Because of $\nabla\zeta^* = 0$ and $\zeta^* \in \mathcal{S}^\perp$ we obtain, for every $v \in V$,

$$\begin{aligned}\langle Av^*, v\rangle = &\int_\Omega \sum_{\nu=1}^m e_\nu'(\cdot, v_\nu^*)\mathbf{S}_\nu \nabla\zeta_\nu^* \cdot \nabla\zeta_\nu \,\mathrm{d}x \\ &+ \sum_{(\alpha,\beta)\in\mathcal{R}} \int_\Omega k_{\alpha\beta} \left(e^{\zeta^*\cdot\alpha} - e^{\zeta^*\cdot\beta}\right)(\alpha-\beta)\cdot\zeta \,\mathrm{d}x = 0,\end{aligned}$$

which means $Av^* = 0$.
3. Let $Av = 0$ and $Ev \in U + \mathcal{U}$ for some $v \in V$. Then

$$0 = \langle Av, v\rangle = \int_\Omega \sum_{\nu=1}^m e_\nu'(\cdot, v_\nu)\mathbf{S}_\nu \nabla\zeta_\nu \cdot \nabla\zeta_\nu \,\mathrm{d}x + \sum_{(\alpha,\beta)\in\mathcal{R}} \int_\Omega k_{\alpha\beta}\left(e^{\zeta\cdot\alpha} - e^{\zeta\cdot\beta}\right)(\alpha-\beta)\cdot\zeta \,\mathrm{d}x.$$

In view of (A2), (A3) and (A4) we obtain $\nabla\zeta = 0$ and $k_{\alpha\beta}\left(e^{\zeta\cdot\alpha} - e^{\zeta\cdot\beta}\right)(\alpha-\beta)\cdot\zeta = 0$, for $(\alpha,\beta) \in \mathcal{R}$. Therefore it follows $\zeta \in \mathcal{S}^\perp$. Since $Ev - Ev^* \in \mathcal{U}$ and $v - v^* \in \mathcal{U}^\perp$ we have

$$\langle Ev - Ev^*, v - v^*\rangle = 0. \tag{23}$$

According to the definition of E this gives

$$\begin{aligned}0 \ = \ &\int_\Omega \mathbf{S}_\varepsilon \nabla(v_0 - v_0^*)\cdot\nabla(v_0 - v_0^*)\,\mathrm{d}x + \int_\Gamma \tau(v_0 - v_0^*)^2\,\mathrm{d}\Gamma \\ + \ &\int_\Omega \sum_{\nu=1}^m \overline{u}_\nu(g_\nu(v_\nu - \overline{v}_\nu) - g_\nu(v_\nu^* - \overline{v}_\nu))(v_\nu - v_\nu^*)\,\mathrm{d}x.\end{aligned}$$

(A2), (A6) then lead to $v_\nu = v_\nu^*$, $\nu = 0, \dots, m$, which completes the proof. □

As in the proof of [10, Lemma 3.4]) we can show the following assertion: If v^* is the minimal point of G_0 then $u^* := Ev^*$ is the unique minimal point of $F|_{U+\mathcal{U}}$.

3 Exponential decay of the free energy

First we prove an estimate of the free energy by the dissipation rate. Let

$$\begin{aligned}\mathcal{M} := \{u \in \mathcal{U} + U :\ &\text{It exists } a \in \partial\mathbb{R}_+^m \text{ such that } a^\alpha = a^\beta \text{ for } (\alpha,\beta)\in\mathcal{R} \\ &\text{and } u_\nu = e_\nu(\cdot, \log a_\nu - q_\nu E_0^{-1}u_0) \text{ if } a_\nu > 0,\ u_\nu = 0 \text{ else},\ \nu = 1,\dots,m\}\end{aligned} \tag{24}$$

and

$$R_\mathcal{M} := \inf_{u\in\mathcal{M}} F(u) \qquad (R_\mathcal{M} = +\infty \text{ if } \mathcal{M} = \emptyset). \tag{25}$$

Remark 3.1 *Obviously, $\mathcal{M} = \emptyset$ if there is no $a \in \partial\mathbb{R}_+^m$ such that $a^\alpha = a^\beta$ for all $(\alpha,\beta) \in \mathcal{R}$. But even if there exists such $a \in \partial\mathbb{R}_+^m$ it may happen that there is no u in $U + \mathcal{U}$ such that $u_\nu = 0 \Longleftrightarrow a_\nu = 0$. In this case the set $\mathcal{M}$ is empty as well.*

Following the proofs of ([10, Lemma 3.5, Lemma 3.7]) and taking into account (21) we obtain the following estimates for the free energy functional.

Lemma 3.1 *Let $u = Ev \in U + \mathcal{U}$ and let (u^*, v^*) be the thermodynamic equilibrium according to Theorem 2.1. Then there are constants $c > 0$ such that*

$$\frac{1}{c}\Big(\|v_0 - v_0^*\|_{H^1}^2 + \sum_{\nu=1}^m \|\sqrt{u_\nu} - \sqrt{u_\nu^*}\|_{L^2}^2\Big) \le F(u) - F(u^*)$$

$$\le c\Big(\|v_0 - v_0^*\|_{H^1}^2 + \sum_{\nu=1}^m \|u_\nu - u_\nu^*\|_{L^2}^2\Big),$$

$$\int_\Omega \sum_{\nu=1}^k u_\nu \log u_\nu \,\mathrm{d}x \le c\,(F(u)+1).$$

Theorem 3.1 *Let* (A1) – (A7) *be fulfilled. Moreover, let $R < R_{\mathcal{M}}$ be fixed, and let (u^*, v^*) be the thermodynamic equilibrium according to Theorem 2.1. Then there exists a constant $c_R > 0$ such that*

$$F(u) - F(u^*) \le c_R D(v) \tag{26}$$

provided that $v \in V$, $u = Ev \in U + \mathcal{U}$, and $F(Ev) \le R$.

Proof. 1. Let $v \in V$ and $a = (\exp(\zeta_1), \dots, \exp(\zeta_m))$. Then

$$\begin{aligned} D(v) &= \int_\Omega \sum_{\nu=1}^m e_\nu'(\cdot, v_\nu)\mathbf{S}_\nu \nabla\zeta_\nu \cdot \nabla\zeta_\nu \,\mathrm{d}x + \int_\Omega \sum_{(\alpha,\beta)\in\mathcal{R}} k_{\alpha\beta}(a^\alpha - a^\beta)(\alpha-\beta)\cdot\zeta \,\mathrm{d}x \\ &\ge \int_\Omega \delta \sum_{\nu=1}^m e_\nu'(\cdot, v_\nu)|\nabla\zeta_\nu|^2 \mathrm{d}x + \int_\Omega \sum_{(\alpha,\beta)\in\mathcal{R}} k_{\alpha\beta}\left(a^{\alpha/2} - a^{\beta/2}\right)^2 \mathrm{d}x =: D_1(v). \end{aligned}$$

Here we used the estimate $(x-y)\log\frac{x}{y} \ge |\sqrt{x} - \sqrt{y}|^2$ for $x, y > 0$. Therefore it suffices to prove the inequality

$$F(u) - F(u^*) \le C D_1(v). \tag{27}$$

2. If (27) would be false, then we find $u_n \in U + \mathcal{U}, v_n \in V, n \in \mathbb{N}$, such that

$$u_n = Ev_n,\ F(u_n) \le R,\ F(u_n) - F(u^*) = C_n D_1(v_n) > 0, \tag{28}$$

and $\lim\limits_{n\to\infty} C_n = +\infty$. Let ζ_n denote the vector of the corresponding electrochemical potentials. Lemma 3.1 and the boundedness results of [13] show that

$$\|v_{n0}\|_{H^1} + \|v_{n0}\|_{L^\infty} + \sum_{\nu=1}^m \|u_{n\nu}\|_{L^1} \le c_1. \tag{29}$$

3. Let $k_\nu = |q_\nu| c_1 + \|\overline{v}_\nu\|_{L^\infty} + \overline{k}_\nu$, $\nu = 1, \dots, m$, where $\overline{k}_\nu > 0$ is such that $g_\nu(\overline{k}_\nu) \ge 1$. Then, for $\zeta_{n\nu} > k_\nu$ we have $v_{n\nu} - \overline{v}_\nu > k_\nu - q_\nu v_{n0} - \overline{v}_\nu > k_\nu - |q_\nu| c_1 - \|\overline{v}_\nu\|_{L^\infty} = \overline{k}_\nu$ which

means $g_\nu(v_{n\nu}-\overline{v}_\nu)>1$ if $(\zeta_{n\nu}-k_\nu)^+>0$ and we can estimate

$$\begin{aligned}
\|\nabla(\zeta_{n\nu}-k_\nu)^+\|^2_{L^2} &\le \int_\Omega \min\{1,g_\nu(v_{n\nu}-\overline{v}_\nu)\}|\nabla(\zeta_{n\nu}-k_\nu)|^2dx\\
&\le \frac{1}{\delta}\int_\Omega g_\nu'(v_{n\nu}-\overline{v}_\nu)|\nabla(\zeta_{n\nu}-k_\nu)|^2dx\\
&\le \frac{1}{\delta}\int_\Omega g_\nu'(v_{n\nu}-\overline{v}_\nu)|\nabla\zeta_{n\nu}|^2dx \le cD_1(v_n)\\
&\le \frac{c}{C_n}(R-F(u^*))\to 0 \text{ as } n\to\infty.
\end{aligned}\tag{30}$$

For $\zeta_{n\nu}\ge k_\nu$ we have $\frac{u_{n\nu}}{\overline{u}_\nu}\ge\widetilde{k}_\nu$ with some $\widetilde{k}_\nu$, $0<\widetilde{k}_\nu<1$. Since $g_n u$ is strongly monotone on $[-a,\infty)$ its inverse is Lipschitzian on $[a,\infty)$, $a>0$ and we find for $\zeta_{n\nu}>k_\nu$

$$|(\zeta_{n\nu}-k_\nu)^+|\le|\zeta_{n\nu}|\le\left|g_\nu^{-1}\big(\frac{u_{n\nu}}{\overline{u}_\nu}\big)+\overline{v}_\nu+q_\nu v_{n0}\right|\le\left|g_\nu^{-1}\big(\frac{u_{n\nu}}{\overline{u}_\nu}\big)-g_\nu^{-1}(1)\right|+c\le c(1+u_{n\nu}).$$

Also for $\zeta_{n\nu}\le k_\nu$ we obtain $|(\zeta_{n\nu}-k_\nu)^+|\le c(1+u_{n\nu})$. Hence $\|(\zeta_{n\nu}-k_\nu)^+\|_{L^1}\le c$ and $\|(\zeta_{n\nu}-k_\nu)^+\|_{H^1}\le c$ (cf. (29) and (30)). Setting $a_{n\nu}:=\exp(\zeta_{n\nu})$ we obtain by Trudinger's imbedding theorem

$$\|a_{n\nu}\|_{L^p}=\|\mathrm{e}^{\zeta_{n\nu}}\|_{L^p}\le\|\mathrm{e}^{k_\nu}\mathrm{e}^{(\zeta_{n\nu}-k_\nu)^+}\|_{L^p}\le c_p,\ \nu=1,\dots,m,\ p\in[1,\infty).$$

Using (A2) and (29) we find

$$\frac{a_{n\nu}}{\sqrt{g_\nu'(v_{n\nu}-\overline{v}_\nu)}}\le\frac{1}{\sqrt{\delta}}\mathrm{e}^{\zeta_{n\nu}}\Big(1+\frac{1}{\sqrt{g_\nu(v_{n\nu}-\overline{v}_\nu)}}\Big)\le c\Big(\mathrm{e}^{\zeta_{n\nu}}+\sqrt{\mathrm{e}^{\zeta_{n\nu}}}\Big)\le c(a_{n\nu}+1).$$

Thus, for $\dfrac{1}{r}=\dfrac{1}{2}+\dfrac{1}{p}$,

$$\begin{aligned}
\|\nabla a_{n\nu}\|_{L^r}=\|a_{n\nu}\nabla\zeta_{n\nu}\|_{L^r}&\le\|\frac{a_{n\nu}}{\sqrt{g_\nu'(v_{n\nu}-\overline{v}_\nu)}}\|_{L^p}\|\sqrt{g_\nu'(v_{n\nu}-\overline{v}_\nu)}\nabla\zeta_{n\nu}\|_{L^2}\\
&\le c\|a_{n\nu}+1\|_{L^p}\,D_1(v_n)^{1/2}.
\end{aligned}\tag{31}$$

The right hand side of (31) converges to 0 as $n\to\infty$ (cf. (30)). Passing to a subsequence if necessary we may assume that

$$a_n\to a \text{ in } W^{1,r}(\Omega;\mathbb{R}^m),\ r\in[1,2),\quad v_{n0}\rightharpoonup v_0 \text{ in } H^1(\Omega)$$

where $\nabla a=0$. In addition we may assume that the sequence (a_n) converges pointwise almost everywhere to a. We check that

$$(a_n^{\alpha/2}-a_n^{\beta/2})^2\to(a^{\alpha/2}-a^{\beta/2})^2 \text{ in } W^{1,r}(\Omega),\ \text{if } r<2.$$

Therefore,

$$\int_\Omega k_{\alpha\beta}(a_n^{\alpha/2}-a_n^{\beta/2})^2\mathrm{d}x\to(a^{\alpha/2}-a^{\beta/2})^2\int_\Omega k_{\alpha\beta}\,\mathrm{d}x.$$

Since, for $(\alpha,\beta)\in\mathcal{R}$,

$$0\le\int_\Omega k_{\alpha\beta}(a_n^{\alpha/2}-a_n^{\beta/2})^2\mathrm{d}x\le D_1(v_n)\le\frac{1}{C_n}(R-F(u^*))\to 0,$$

we have necessarily

$$a^\alpha=a^\beta\quad\forall(\alpha,\beta)\in\mathcal{R}. \tag{32}$$

4. Due to $0<g_\nu'(\theta)\le\delta^{-1}g_\nu(\theta)\le\delta^{-2}\mathrm{e}^\theta$ we can estimate by the generalized mean value theorem

$$\frac{|g_\nu(x)-g_\nu(y)|}{|\mathrm{e}^x-\mathrm{e}^y|}\le\sup_{\theta\in[x,y]}\frac{g_\nu'(\theta)}{\mathrm{e}^\theta}\le c. \tag{33}$$

We introduce

$$u_\nu:=e_\nu(\cdot,\log(a_\nu)-q_\nu v_0)\text{ if }a_\nu\ne 0,\quad u_\nu:=0\text{ if }a_\nu=0. \tag{34}$$

If $u_\nu\ne 0$ then by (33)

$$\begin{aligned}|u_{n\nu}-u_\nu| &\le c|g_\nu(\log(a_{n\nu})-q_\nu v_{n0}-\overline{v}_\nu)-g_\nu(\log(a_\nu)-q_\nu v_0-\overline{v}_\nu)|\\ &\le c|\exp(\log(a_{n\nu})-q_\nu v_{n0}-\overline{v}_\nu)-\exp(\log(a_\nu)-q_\nu v_0-\overline{v}_\nu)|\\ &\le c(|a_{n\nu}-a_\nu|+(a_{n\nu}+1)|v_{n0}-v_0|).\end{aligned} \tag{35}$$

Such an estimate for $|u_{n\nu}-u_\nu|$ is true also if $u_\nu=0$. Since the right hand side of (35) converges to 0 in $L^p(\Omega)$ for every finite p as n tends to ∞, we have

$$u_{n\nu}\to u_\nu\text{ in }L^p(\Omega),\quad p\in[1,\infty).$$

5. We set $u_0:=\sum_{\nu=1}^m q_\nu u_\nu$ and $u:=(u_0,u_1,\dots,u_m)$. Because of $u_n-U\in\mathcal{U}$ and $E_0v_{n0}=u_{n0}$ we obtain by passing to the limit $u-U\in\mathcal{U}$ and $E_0v_0=u_0$. The operator $E_0^{-1}:H^1(\Omega)^*\to H^1(\Omega)$ is Lipschitzian because of being the inverse of a strongly monotone operator. Therefore, $v_{n0}=E_0^{-1}u_{n0}\to v_0$ in $H^1(\Omega)$. Moreover, due to the lower semicontinuity of F on V^*,

$$F(u)\le\liminf_{n\to\infty}F(u_n)\le R<R_{\mathcal{M}}.$$

Thus, $u\notin\mathcal{M}$ (see (24), (25)). This is possible only if $a_\nu>0$, $\nu=1,\dots,m$. Defining $\zeta_\nu:=\log(a_\nu)$, $v_\nu:=\zeta_\nu-q_\nu v_0$, $\nu=1,\dots,m$, we get $v:=(v_0,v_1,\dots,v_m)\in V$, $u=Ev\in U+\mathcal{U}$, and $Av=0$. By Theorem 2.1 we conclude that $v=v^*$ and $u=u^*$.

6. Due to the convergence properties of the sequences (v_{n0}) and (u_n) we have (see Lemma 3.1)

$$\lambda_n:=\sqrt{F(u_n)-F(u^*)}\to 0\text{ as }n\to\infty. \tag{36}$$

Additionally (according to (28)) we find

$$\frac{1}{C_n}=\frac{1}{\lambda_n^2}D_1(v_n)=\int_\Omega\Big(\delta\sum_{\nu=1}^m e_\nu'(\cdot,v_{n\nu})\left|\frac{\nabla\zeta_{n\nu}}{\lambda_n}\right|^2+\sum_{(\alpha,\beta)\in\mathcal{R}}\frac{k_{\alpha\beta}}{\lambda_n^2}\left(a_n^{\alpha/2}-a_n^{\beta/2}\right)^2\Big)\mathrm{d}x. \tag{37}$$

We introduce the quantities

$$\widetilde{v}_{n0}:=\frac{1}{\lambda_n}(v_{n0}-v_0),\quad\widetilde{u}_n:=\frac{1}{\lambda_n}(u_n-u),\quad b_{n\nu}:=\frac{1}{\lambda_n}\Big(\sqrt{\frac{a_{n\nu}}{a_\nu}}-1\Big),\ \nu=1,\dots,m.$$

Lemma 3.1 ensures that $\|\widetilde{v}_{n0}\|_{H^1} \le c$. Because of (34), $u_{n\nu} = e_\nu(\cdot, \log(a_{n\nu}) - q_\nu v_{n0})$, $e_\nu(\cdot, y) \le c\,\mathrm{e}^y$, $\|a_{n\nu}\|_{W^{1,r}} \le c$ and $\|v_{n0}\|_{H^1} \le c$ we estimate

$$\begin{aligned}
\|\widetilde{u}_{n\nu}\|_{L^{3/2}} &= \|\frac{1}{\lambda_n}(\sqrt{u_{n\nu}} - \sqrt{u_\nu})(\sqrt{u_{n\nu}} + \sqrt{u_\nu})\|_{L^{3/2}} \\
&\le \|\frac{1}{\lambda_n}(\sqrt{u_{n\nu}} - \sqrt{u_\nu})\|_{L^2}\|(\sqrt{u_{n\nu}} + \sqrt{u_\nu})\|_{L^6} \le c.
\end{aligned}$$

We have

$$\begin{aligned}
|a_{n\nu} - a_\nu| &= \left|\exp\left(g_\nu^{-1}\left(\frac{u_{n\nu}}{\overline{u}_\nu}\right) + \overline{v}_\nu + q_\nu v_{n0}\right) - \exp\left(g_\nu^{-1}\left(\frac{u_\nu}{\overline{u}_\nu}\right) + \overline{v}_\nu + q_\nu v_0\right)\right| \\
&\le c(a_{n\nu}+1)\frac{|u_{n\nu} - u_\nu|}{\overline{u}_\nu} + c|v_{n0} - v_0|.
\end{aligned}$$

Therefore,

$$\|b_{n\nu}\|_{L^1} \le c\|a_{n\nu}+1\|_{L^3}\|\widetilde{u}_{n\nu}\|_{L^{3/2}} + c\|\widetilde{v}_{n0}\|_{H^1}.$$

Using

$$\nabla b_{n\nu} = \frac{1}{2\lambda_n}\sqrt{\frac{a_{n\nu}}{a_\nu}}\nabla\zeta_{n\nu} = \frac{1}{2\lambda_n}\sqrt{\frac{a_{n\nu}}{a_\nu g_\nu'(v_{n\nu} - \overline{v}_\nu)}}\sqrt{g_\nu'(v_{n\nu} - \overline{v}_\nu)}\nabla\zeta_{n\nu}$$

and

$$\frac{a_{n\nu}}{g_\nu'(v_{n\nu} - \overline{v}_\nu)} \le \frac{1}{\delta}\mathrm{e}^{\zeta_{n\nu}}\Big(1 + \frac{1}{g_\nu(v_{n\nu} - \overline{v}_\nu)}\Big) \le c\mathrm{e}^{\zeta_{n\nu}}\big(1 + \frac{1}{e^{\zeta_{n\nu}}}\big) \le c(a_{n\nu}+1)$$

we find

$$\|\nabla b_{n\nu}\|_{L^r} \le c\|a_{n\nu}+1\|_{L^p}\left\|\frac{\sqrt{g_\nu'(v_{n\nu} - \overline{v}_\nu)}\nabla\zeta_{n\nu}}{\lambda_n}\right\|_{L^2} \le \frac{c}{C_n}$$

provided that $\frac{1}{r} = \frac{1}{2} + \frac{1}{p}$. By means of (35) we obtain

$$|\widetilde{u}_{n\nu}| \le c\left|\frac{a_{n\nu} - a_\nu}{\lambda_n}\right| + c(a_{n\nu}+1)|\widetilde{v}_{n0}| \le c(\sqrt{a_{n\nu}} + \sqrt{a_\nu})|b_{n\nu}| + c(a_{n\nu}+1)|\widetilde{v}_{n0}|. \tag{38}$$

In summary, the preceding estimates show that, passing to a subsequence if necessary, we may assume that

$$\begin{gathered}
b_{n\nu} \to b_\nu \text{ in } W^{1,r}(\Omega),\ r < 2, \\
\widetilde{v}_{n0} \rightharpoonup \widetilde{v}_0 \text{ in } H^1(\Omega),\ \ \widetilde{u}_n \rightharpoonup \widetilde{u} \text{ in } L^p(\Omega, \mathbb{R}^{m+1}),\ \ p \in [1,\infty),
\end{gathered}$$

and that the sequences $(b_{n\nu})$, $(\widetilde{v}_{n0})$ converge pointwise almost everywhere in Ω.

7. In view of $u_n - U \in \mathcal{U}$ we have $\frac{1}{\lambda_n}(u_n - u) \in \mathcal{U}$. Passing to the limit we find that $\widetilde{u} \in \mathcal{U}$. In particular,

$$\Big(\int_\Omega \widetilde{u}_1\,\mathrm{d}x, \dots, \int_\Omega \widetilde{u}_m\,\mathrm{d}x\Big) \in \mathcal{S}. \tag{39}$$

By the definition of $b_{n\nu}$ we have, for $(\alpha,\beta) \in \mathcal{R}$,

$$\begin{aligned}
a^{-\alpha}\left(a_n^{\alpha/2} - a_n^{\beta/2}\right)^2 &= \Big(\prod_{\nu=1}^m(\lambda_n b_{n\nu}+1)^{\alpha_\nu} - \prod_{\nu=1}^m(\lambda_n b_{n\nu}+1)^{\beta_\nu}\Big)^2 \\
&= \Big(\lambda_n\sum_{\nu=1}^m b_{n\nu}(\alpha_\nu - \beta_\nu)\Big)^2 + Q_n,
\end{aligned} \tag{40}$$

where

$$|Q_n| \le c\lambda_n^3(|b_n|+1)^{p_0}, \qquad 0 \le p_0 \le 2 \max_{(\alpha,\beta)\in\mathcal{R}} \max\Big\{\sum_{\nu=1}^m \alpha_\nu, \sum_{\nu=1}^m \beta_\nu\Big\}.$$

Taking into account that $\lambda_n \to 0$ as $n \to \infty$, we obtain

$$\frac{1}{\lambda_n^2}\|Q_n\|_{L^1} \le c\lambda_n \int_\Omega (|b_n|+1)^{p_0}\,\mathrm{d}x \to 0 \text{ as } n \to \infty.$$

This result together with (37) and (40) gives

$$\lim_{n\to\infty} \int_\Omega k_{\alpha\beta}\Big(\sum_{\nu=1}^m b_{n\nu}(\alpha_\nu - \beta_\nu)\Big)^2 \mathrm{d}x = 0 \quad \forall(\alpha,\beta) \in \mathcal{R}.$$

Hence

$$b := (b_1, \dots, b_m) \in \mathcal{S}^\perp. \tag{41}$$

8. Letting $n \to \infty$ in

$$\widetilde{u}_{n\nu} = \frac{\overline{u}_\nu}{\lambda_n}\Big(g_\nu(\log(a_{n\nu}) - q_\nu v_{n0} - \overline{v}_\nu) - g_\nu(\log(a_\nu) - q_\nu v_0 - \overline{v}_\nu)\Big)$$

we find

$$\widetilde{u}_\nu = \overline{u}_\nu g_\nu'(\log(a_\nu) - q_\nu v_0 - \overline{v}_\nu)(2b_\nu - q_\nu\widetilde{v}_0) = \overline{u}_\nu g_\nu'(v_\nu - \overline{v}_\nu)(2b_\nu - q_\nu\widetilde{v}_0). \tag{42}$$

The equations satisfied by v_{n0} and v_0, respectively, imply that, for some $\gamma > 0$,

$$\gamma\|v_{n0} - v_0\|_{H^1}^2 \le \langle E_0 v_{n0} - E_0 v_0, v_{n0} - v_0\rangle = \sum_{\nu=1}^m \int_\Omega q_\nu(u_{n\nu} - u_\nu)(v_{n0} - v_0)\,\mathrm{d}x. \tag{43}$$

Dividing by λ_n^2 and passing to the limit as $n \to \infty$, we obtain,

$$\gamma\|\widetilde{v}_0\|_{H^1}^2 \le \sum_{\nu=1}^m \int_\Omega q_\nu \widetilde{u}_\nu \widetilde{v}_0\,\mathrm{d}x.$$

Using (39), (41), and (42) we derive from this inequality that

$$\gamma\|\widetilde{v}_0\|_{H^1}^2 \le \sum_{\nu=1}^m \int_\Omega \widetilde{u}_\nu(q_\nu\widetilde{v}_0 - 2b_\nu)\,\mathrm{d}x = -\sum_{\nu=1}^m \int_\Omega \overline{u}_\nu g_\nu'(v_\nu - \overline{v}_\nu)(q_\nu\widetilde{v}_0 - 2b_\nu)^2 \mathrm{d}x \le 0.$$

Thus it follows $\widetilde{v}_0 = 0$, $b = 0$, and $\widetilde{u} = 0$.

9. Dividing (43) by λ_n^2 we find that $\widetilde{v}_{n0} \to \widetilde{v}_0 = 0$ in $H^1(\Omega)$. By (38)

$$|\widetilde{u}_{n\nu}| \le c(\sqrt{a_{n\nu}} + 1)|b_{n\nu}| + c(a_{n\nu} + 1)|\widetilde{v}_{n0}|.$$

Hence $\widetilde{u}_n \to 0$ in $L^p(\Omega, \mathbb{R}^{m+1})$, $p \in [1, \infty)$. By the definition of λ_n (see (36)) and Lemma 3.1

$$1 = \frac{1}{\lambda_n^2}(F(u_n) - F(u^*)) \le c\Big(\|\widetilde{v}_{n0}\|_{H^1}^2 + \sum_{\nu=1}^m \|\widetilde{u}_{n\nu}\|_{L^2}^2\Big).$$

Because of the preceding results the right hand side converges to 0 as $n \to \infty$. This contradiction shows that the assumption made in the beginning of the second step of the proof was wrong, i.e., (27) holds, and the proof is complete. □

Now we are able to prove the exponential decay of the free energy to its equilibrium value.

Theorem 3.2 *Let* (A1) – (A7) *be fulfilled, let* (u, v) *be a solution to the initial value problem* (16)*, and let* (u^*, v^*) *be the thermodynamic equilibrium. We suppose that* $F(U) < R_{\mathcal{M}}$*. Then there exists* $\lambda > 0$ *such that*

$$F(u(t)) - F(u^*) \le e^{-\lambda t}(F(U) - F(u^*)) \quad \forall\, t \ge 0.$$

Proof. If (u, v) is a solution to (16), then $v(t) \in \partial F(u(t))$ for a.e. $t \in \mathbb{R}_+$, and according to [1, Lemma 3.3] we obtain for $\lambda \in \mathbb{R}$

$$\begin{aligned} &\mathrm{e}^{\lambda t}(F(u(t)) - F(u^*)) - (F(U) - F(u^*)) \\ &\quad = \int_0^t \mathrm{e}^{\lambda s}\Big\{\lambda(F(u(s)) - F(u^*)) + \langle u'(s), v(s)\rangle\Big\}\,\mathrm{d}s \\ &\quad = \int_0^t \mathrm{e}^{\lambda s}\Big\{\lambda(F(u(s)) - F(u^*)) - \langle A(v(s)), v(s)\rangle\Big\}\,\mathrm{d}s \\ &\quad = \int_0^t \mathrm{e}^{\lambda s}\Big\{\lambda(F(u(s)) - F(u^*)) - D(v(s))\Big\}\,\mathrm{d}s. \end{aligned} \tag{44}$$

Setting in (44) $\lambda = 0$, we get $F(u(t)) \le F(U) < R_{\mathcal{M}}$ for all $t \in \mathbb{R}_+$. Since $v(s) \in V$, $u(s) = Ev(s) \in U + \mathcal{U}$ f.a.a. $s \in \mathbb{R}_+$ we conclude by Theorem 3.1 that

$$F(u(s)) - F(u^*) \le c_R\, D(v(s)) \quad \text{f.a.a. } s \in \mathbb{R}_+.$$

Thus (44) with $\lambda = 1/c_R$ proves the theorem. □

Remark 3.2 *We obtained for general electro-reaction-diffusion systems the exponential decay of the free energy to its equilibrium value by an indirect proof. Therefore we did not get an explicit rate of convergence. But we took into account heterostructures, anisotropies, a wide class of statistics and any final set of reversible reactions.*

There are papers where for special situations an explicit rate of convergence is proved. Gajewski and Gärtner [4] did this for the van Roosbroeck system with magnetic field. Desvillettes and Fellner [3] provide an explicit rate of convergence for a reaction-diffusion system of two species and the reaction $2X_1 \rightleftharpoons X_2$ *and one invariant and for a system of three species, the reaction* $X_1 + X_2 \rightleftharpoons X_3$ *and two invariants, respectively.*

Remark 3.3 *In [9] it is demonstrated how results concerning steady states and energy estimates for electro-reaction-diffusion systems can be carried over to reduced system arising for the limit case that some of the kinetic subprocesses are very fast. There for all species Boltzmann statistics is assumed and no anisotropies are considered. But the essential ideas slightly modified can also be applied in our more complicated situation.*

4 Discretized problems

4.1 Time discretization

Theorem 4.1 *Let* (A1) – (A7) *be fulfilled, let* (u^*, v^*) *be the thermodynamic equilibrium and let* $h > 0$. *Then the implicit time discretization scheme*

$$\begin{aligned} &u(nh) - u\big((n-1)h\big) + hAv(nh) = 0, \quad u(nh) = Ev(nh), \quad n \geq 1, \\ &u(0) = U, \quad v(nh) \in V, \quad n \geq 0 \end{aligned} \tag{45}$$

is dissipative. Moreover, if $F(U) \leq R < R_{\mathcal{M}}$. *Then there exists* $\lambda > 0$ *such that*

$$F\big(u(nh)\big) - F(u^*) \leq e^{-\lambda nh}\big(F(U) - F(u^*)\big) \quad \forall n \geq 1.$$

Proof. 1. A Solution to the time discrete problem (45) fulfills the invariance property

$$u(nh) - U \in \mathcal{U}, \quad n \geq 1.$$

The discrete problem has the same steady state (u^*, v^*) as the continuous problem (16).
2. F is subdifferentiable in arguments u, where $u_\nu > 0$, $\nu = 1, \dots, m$. If $u = Ev$, then $u \in \partial G(v)$ and $v \in \partial F(u)$ and we obtain the inequality

$$F(w) - F(u) \geq \langle v, w - u \rangle \quad \forall w \in V^*. \tag{46}$$

3. We shortly write u^n, v^n for $u(nh)$, $v(nh)$, $n \geq 0$. Let $n_2 > n_1 \geq 0$ and $\lambda \geq 0$. Using $u^l = Ev^l$, (46) and the relation $D(v^l) = \langle Av^l, v^l \rangle$ we estimate

$$\begin{aligned} &\mathrm{e}^{\lambda n_2 h}\Big(F(u^{n_2}) - F(u^*)\Big) - \mathrm{e}^{\lambda n_1 h}\Big(F(u^{n_1}) - F(u^*)\Big) \\ &\quad = \sum_{l=n_1+1}^{n_2} \mathrm{e}^{\lambda(l-1)h}\Big\{(\mathrm{e}^{\lambda h} - 1)\big(F(u^l) - F(u^*)\big) + \big(F(u^l) - F(u^{l-1})\big)\Big\} \\ &\quad \leq \sum_{l=n_1+1}^{n_2} h\, \mathrm{e}^{\lambda(l-1)h}\Big\{\mathrm{e}^{\lambda h}\lambda\big(F(u^l) - F(u^*)\big) - D(v^l)\Big\}. \end{aligned} \tag{47}$$

4. Since $D(v) \geq 0$ for $v \in V$, we obtain by setting $\lambda = 0$ in (47) that

$$F(u^{n_2}) \leq F(u^{n_1}) \leq F(U) \leq R < R_{\mathcal{M}} \quad \forall n_2 \geq n_1 \geq 0.$$

Because of $F(u^l) \leq R < R_{\mathcal{M}}$, $u^l = Ev^l \in U + \mathcal{U}$ for $l \geq 1$, Theorem 3.1 supplies a $c_R > 0$ such that (26) is fulfilled. Choosing now $\lambda > 0$ such that $\lambda \mathrm{e}^{\lambda h} c_R < 1$ and $n_1 = 0$, the estimate (47) proves the theorem. $\square$

4.2 Space discretization

For our further considerations we set $\overline{v}_\nu = 0$, $\nu = 1, \dots, m$. Moreover, in a first step we assume a 2D structure with constant material parameters $\overline{u}_\nu$, $k_{\alpha\beta}$, $\mathbf{S}_\nu$, $\mathbf{S}_\varepsilon$.

Let a Delaunay grid with M grid points $\{x^k : x^k \in \overline{\Omega}, k = 1, \dots, M\}$ be given. We use the following sets of indeces

$$\mathcal{V} := \Big\{k : x^k \in \overline{\Omega}\}, \quad \mathcal{T} := \{k : x^k \in \overline{\Omega} \setminus \Omega\Big\}.$$

Due to (3), (7), (A3) and (A6) the anisotropy matrices $\mathbf{S}_\nu$ are invertible 2×2 matrices. For $x, y \in \overline{\Omega}$ we introduce new distances defined via the anisotropy matrices $\mathbf{S}_\nu$,

$$d_\nu(x, y) := \sqrt{(x-y)^T \mathbf{S}_\nu^{-1}(x-y)}, \quad \nu = 0, \dots, m.$$

By means of these we define anisotropic Voronoi cells for each species (see Labelle and Shewchuk [14])

$$V_\nu^k = \Big\{x \in \overline{\Omega} : d_\nu(x, x^k) \le d_\nu(x, x^l) \quad \forall l \in \mathcal{V}\Big\}, \ \nu = 0, \dots, m, \ k \in \mathcal{V}.$$

Remark 4.1 *1. Note that since $\mathbf{S}_\nu$ are constant the sets $\partial V_\nu^k \cap \partial V_\nu^l$ are parts of straight lines or they are empty. Only if the points are directly neighbored the sets have positive measure.*
2. For $y \in K_\nu^{kl} := \{y : d_\nu(x^k, y) = d_\nu(x^l, y)\}$ we have

$$2\big(y, \mathbf{S}_\nu^{-1}(x^k - x^l)\big) = (x^k, \mathbf{S}_\nu^{-1} x^k) - (x^l, \mathbf{S}_\nu^{-1} x^l),$$

thus

$$\big(y - z, \mathbf{S}_\nu^{-1}(x^k - x^l)\big) = 0 \quad \forall\, y = \begin{pmatrix} y_1 \\ y_2 \end{pmatrix}, z = \begin{pmatrix} z_1 \\ z_2 \end{pmatrix} \in K_\nu^{kl}. \tag{48}$$

The vector $(y_2 - z_2, z_1 - y_1)^T$ is parallel to the normal vector n_ν^{kl} to K_ν^{kl}. And $(x_2^k - x_2^l, x_1^l - x_1^k)^T$ is orthogonal to $x^k - x^l$. Since $\mathbf{S}_\nu$ is an invertible 2×2 matrix, (48) implies

$$\left(\mathbf{S}_\nu \begin{pmatrix} y_2 - z_2 \\ z_1 - y_1 \end{pmatrix}, \begin{matrix} x_2^k - x_2^l \\ x_1^l - x_1^k \end{matrix} \right) = 0.$$

Thus, the construction guarantees that the vector $\mathbf{S}_\nu n_\nu^{kl}$ is parallel to $x^k - x^l$. For directly neighbored points x^k and x^l we denote the (outer) normal vector on V_ν^k at $\partial V_\nu^k \cap \partial V_\nu^l$ by n_ν^{kl}, and $\nu = 0, \dots, m$ too.

3. Moreover, the neighborhood relations can differ from species to species due to the different anisotropies.

For $k \in \mathcal{V}$ we denote by u_ν^k and u_0^k we the mass of the ν-th species in V_ν^k and the charge in V_ε^k, respectively. Taking into account that the Voronoi cells can differ for the different species, the relation (10) has to be substituted for the discrete situation by

$$u_0^k = \sum_{\nu=1}^m q_\nu \sum_{l \in \mathcal{V}} \frac{|V_\varepsilon^k \cap V_\nu^l|}{|V_\nu^l|} u_\nu^l. \tag{49}$$

Associated to the grid points we have electrostatic potentials v_0^k, chemical potentials v_ν^k and electrochemical potentials ζ_ν^k, $\nu = 1, \ldots, m$. The discrete version of the state equations (1) then is

$$u_\nu^k = \overline{u}_\nu g_\nu(v_\nu^k)|V_\nu^k|, \quad k \in \mathcal{V}\,,\; \nu = 1, \ldots, m. \tag{50}$$

Electrochemical potentials are determined by

$$\zeta_\nu^k = v_\nu^k + q_\nu \sum_{l \in \mathcal{V}} \frac{|V_\varepsilon^l \cap V_\nu^k|}{|V_\nu^k|} v_0^l, \quad k \in \mathcal{V}\,,\; \nu = 1, \ldots, m. \tag{51}$$

The discrete version of the Poisson equation (6) is obtained by testing with the characteristic function of V_ε^k and using Gauss theorem. We obtain

$$-\sum_{l \in \mathcal{V}} \frac{v_0^l - v_0^k}{|x^l - x^k|} |\mathbf{S}_\varepsilon n_\varepsilon^{kl}||\partial V_\varepsilon^k \cap \partial V_\varepsilon^l| + \tau v_0^k |\partial V_\varepsilon^k \cap \Gamma| - f^k = u_0^k, \quad k \in \mathcal{V}, \tag{52}$$

where

$$f^k = \int_{V_\varepsilon^k} f \,\mathrm{d}x + \int_{\partial V_\varepsilon^k \cap \Gamma} f^\Gamma \,\mathrm{d}\Gamma.$$

In order to find a space discrete version of the drift-diffusion term in the continuity equations (5), we again use Gauss theorem and write for $k \in \mathcal{V} \setminus \mathcal{T}$

$$\int_{V_\nu^k} \nabla \cdot j_\nu \,\mathrm{d}x = \sum_{l \in \mathcal{V}} \int_{\partial V_\nu^k \cap \partial V_\nu^l} j_\nu \cdot n_\nu^{kl} \,\mathrm{d}\Gamma \approx \sum_{l \in \mathcal{V}} J_\nu^{kl} |\partial V_\nu^k \cap \partial V_\nu^l|.$$

The approximation of the flux $j_\nu \cdot n_\nu^{kl}$ of the ν-th species across $\partial V_\nu^k \cap \partial V_\nu^l$ is done by

$$\begin{aligned}
\int_{\partial V_\nu^k \cap \partial V_\nu^l} j_\nu \cdot n_\nu^{kl} \,\mathrm{d}\Gamma &= -\int_{\partial V_\nu^k \cap \partial V_\nu^l} \mathbf{S}_\nu \overline{u}_\nu g_\nu'(v_\nu) \nabla \zeta_\nu \cdot n_\nu^{kl} \,\mathrm{d}\Gamma \\
&= -\int_{\partial V_\nu^k \cap \partial V_\nu^l} \overline{u}_\nu g_\nu'(v_\nu) \nabla \zeta_\nu \cdot \mathbf{S}_\nu n_\nu^{kl} \,\mathrm{d}\Gamma \\
&\approx -\overline{u}_\nu \, Z_\nu^{kl} \, \frac{\zeta_\nu^l - \zeta_\nu^k}{|x^l - x^k|} \, |\mathbf{S}_\nu n_\nu^{kl}||\partial V_\nu^k \cap \partial V_\nu^l| \\
&=: J_\nu^{kl} |\partial V_\nu^k \cap \partial V_\nu^l|,
\end{aligned}$$

where

$$Z_\nu^{kl} = \begin{cases} \frac{g_\nu(v_\nu^l) - g_\nu(v_\nu^k)}{v_\nu^l - v_\nu^k} & \text{for } v_\nu^l \neq v_\nu^k \\ g_\nu'(v_\nu^k) & \text{for } v_\nu^l = v_\nu^k \end{cases}. \tag{53}$$

Since homogeneous Neumann boundary conditions for the continuity equations are included, we end up with the following discrete version of the continuity equations (5), considering the anisotropic Voronoi cells V_ν^k

$$u_\nu^{k\prime} + \sum_{l \in \mathcal{V}} J_\nu^{kl} |\partial V_\nu^k \cap \partial V_\nu^l| - R_\nu^k = 0, \quad k \in \mathcal{V}\,,\; \nu = 1, \ldots, m, \tag{54}$$

where the source terms R_ν^k have to be calculated by

$$R_\nu^k = \sum_{\alpha,\beta\in\mathcal{R}} (\beta_\nu - \alpha_\nu) \sum_{k_1\in\mathcal{V}} \cdots \sum_{k_{\nu-1}\in\mathcal{V}} \sum_{k_{\nu+1}\in\mathcal{V}} \cdots \sum_{k_m\in\mathcal{V}} R_{\alpha\beta}\big[\zeta_1^{k_1},\dots,\zeta_{\nu-1}^{k_{\nu-1}},\zeta_\nu^k,\zeta_{\nu+1}^{k_{\nu+1}},\dots,\zeta_m^{k_m}\big]$$
$$\times |V_1^{k_1}\cap\cdots\cap V_{\nu-1}^{k_{\nu-1}}\cap V_\nu^k\cap V_{\nu+1}^{k_{\nu+1}}\cap\cdots\cap V_m^{k_m}|$$

with

$$R_{\alpha\beta}\big[\zeta_1^{k_1},\dots,\zeta_m^{k_m}\big] = k_{\alpha\beta}\Big(\mathrm{e}^{\sum_{\nu=1}^m \alpha_\nu\zeta_\nu^{k_\nu}} - \mathrm{e}^{\sum_{\nu=1}^m \beta_\nu\zeta_\nu^{k_\nu}}\Big) \tag{55}$$

and the expression for ζ_ν^k given in (51).

We use the notation

$$\vec u = (\vec u_0,\dots,\vec u_m),\quad \vec v = (\vec v_0,\dots,\vec v_m),\quad \vec u_\nu = \big(u_\nu^k\big)_{k\in\mathcal{V}},\quad \vec v_\nu = \big(v_\nu^k\big)_{k\in\mathcal{V}},\quad \nu=0,\dots,m.$$

The equations (52) form a system of linear equations

$$P\vec v_0 - \vec f = \vec u_0,\quad \text{where } \vec f = \big(f^k\big)_{k=1,\dots,M}.$$

Lemma 4.1 *We assume* (A1) *and* (A6)*. Moreover, let* $\mathbf{S}_\varepsilon$ *and* τ *be constant. Then for arbitrarily given* $\vec u_0$ *,* $\vec f\in\mathbb{R}^M$ *there exists a unique solution* $\vec v_0\in\mathbb{R}^M$ *to* $P\vec v_0 - \vec f = \vec u_0$*.*

Proof. The $M\times M$ matrix P is symmetric. Moreover, since $\tau>0$ (see (A6)) the relation $(P\vec w_0,\vec w_0)=0$ implies $\vec w_0 = 0$. Here we argue as follows: Let

$$\begin{aligned} 0 &= (P\vec w_0,\vec w_0)\\ &= -\sum_{k\in\mathcal{V}}\Big(\sum_{l\in\mathcal{V}}\frac{w_0^l-w_0^k}{|x^l-x^k|}|\mathbf{S}_\varepsilon n_\varepsilon^{kl}||\partial V_\varepsilon^k\cap\partial V_\varepsilon^l|w_0^k + \tau\,(w_0^k)^2|\partial V_\varepsilon^k\cap\Gamma|\Big)\\ &= \sum_{k,l\in\mathcal{V},\,l\le k}\frac{(w_0^l-w_0^k)^2}{|x^l-x^k|}|\mathbf{S}_\varepsilon n_\varepsilon^{kl}||\partial V_\varepsilon^k\cap\partial V_\varepsilon^l| + \sum_{k\in\mathcal{V}}\tau\,(w_0^k)^2|\partial V_\varepsilon^k\cap\Gamma|. \end{aligned}$$

Then $w_0^k=0$ for all $k\in\mathcal{T}$. For all $\widehat k\in\mathcal{V}$ we find a finite path of neighboring Voronoi cells starting at $V_\varepsilon^{\widehat k}$ and ending at a $V_\varepsilon^{k^*}$, $k^*\in\mathcal{T}$, which can be used in opposite direction to show cell by cell that the corresponding $w_0^k=0$ and finally $w_0^{\widehat k}=0$, too. In summary, zero is not an eigenvalue of P and the matrix P is regular. □

4.3 Discrete energy functionals

First, we define as a discrete version of E (cf. (13)) the operator $\widehat E\colon \mathbb{R}^{M(m+1)}\to\mathbb{R}^{M(m+1)}$,

$$\widehat E\vec v = \Big(P\vec v_0 - \vec f, \Big(\big(\overline u_\nu g_\nu(v_\nu^k)|V_\nu^k|\big)_{k\in\mathcal{V}}\Big)_{\nu=1,\dots,m}\Big)$$

and obtain the corresponding discrete potential $\widehat G\colon\mathbb{R}^{M(m+1)}\to\mathbb{R}$,

$$\widehat G(\vec v) = \frac12(P\vec v_0,\vec v_0) - (\vec f,\vec v_0) + \sum_{\nu=1}^m\sum_{k\in\mathcal{V}}\overline u_\nu|V_\nu^k|\int_0^{v_\nu^k} g_\nu(y)\,\mathrm{d}y.$$

As in (18), (19) we introduce the discrete free energy $\widehat{F}$ as the conjugate functional,

$$\widehat{F}(\vec{u}) = \sup_{\vec{v}\in\mathbb{R}^{M(m+1)}} \big\{(\vec{u},\vec{v}) - \widehat{G}(\vec{v})\big\}.$$

Then again, $\widehat{F} : \mathbb{R}^{M(m+1)} \to \overline{\mathbb{R}}$ is convex and lower semicontinuous. $\widehat{F}$ is differentiable in arguments $\vec{u}$, where $\vec{u_\nu} > 0$, $\nu = 1,\dots,m$. If $\vec{u} = \widehat{E}\vec{v}$, then $\vec{u} = \widehat{G}'(\vec{v})$ and $\vec{v} = \widehat{F}'(\vec{u})$. In particular we obtain for $\vec{u} = \widehat{E}\vec{v}$, $\vec{v} \in \mathbb{R}^{M(m+1)}$ the inequality

$$\widehat{F}(\vec{w}) - \widehat{F}(\vec{u}) \geq \widehat{F}'(\vec{u})\cdot(\vec{w}-\vec{u}) \quad \forall \vec{w} \in \mathbb{R}^{M(m+1)}, \tag{56}$$

which will be used to show that our discretization scheme (Euler backward in time and space discretization of the Poisson equation and the continuity equations as described in Theorem 4.2 below) is dissipative. Moreover, for $\vec{u} = \widehat{E}\vec{v}$ we calculate

$$\begin{aligned}\widehat{F}(\vec{u}) &= (\widehat{E}\vec{v},\vec{v}) - \widehat{G}(\vec{v})\\ &= \frac{1}{2}(P\vec{v}_0,\vec{v}_0) + \sum_{\nu=1}^{m}\sum_{k\in\mathcal{V}} \overline{u}_\nu |V_\nu^k| \Big(g_\nu(v_\nu^k)v_\nu^k - \int_0^{v_\nu^k} g_\nu(y)\,\mathrm{d}y\Big).\end{aligned}$$

4.4 Dissipativity of the discretization scheme

We define discrete initial values

$$U_\nu^k := \int_{V_\nu^k} U_\nu \,\mathrm{d}x, \quad k \in \mathcal{V}\,,\ \nu = 1,\dots,m.$$

U_0^k is calculated via (49), where the u_ν^k have to be substituted by U_ν^k.

Theorem 4.2 *We assume* (A1) – (A6)*. Moreover, let* $\overline{v}_\nu = 0$ *and let* $\overline{u}_\nu$, $\mathbf{S}_\nu$, $k_{\alpha\beta}$, $\mathbf{S}_\varepsilon$ *and* τ *be constant. Let* $h > 0$ *be given. The following discrete version of* (5), (6) *is dissipative*

$$\begin{aligned} P\vec{v}_0(nh) - \vec{f} &= \vec{u}_0(nh), \quad n \geq 0,\\ \frac{\vec{u}_\nu^k(nh) - \vec{u}_\nu^k((n-1)h)}{h} &= -\sum_{l\in\mathcal{V}} J_\nu^{kl}(nh)|\partial V_\nu^k \cap \partial V_\nu^l| + R_\nu^k(nh),\\ &\qquad k\in\mathcal{V},\ n\geq 1,\ \nu = 1,\dots,m,\\ u_\nu^k(0) &= U_\nu^k, \quad k \in \mathcal{V},\ \nu = 0,\dots,m.\end{aligned}$$

Proof. Let $n \in \mathbb{N}$ be arbitrarily fixed. For $\vec{u}\big((n-1)h\big)$ we write $\vec{u}^{\,\mathrm{old}}$, for quantities used at time $t = nh$ we leave the time argument. Using (56) and (49) we can estimate

$$\begin{aligned}
\widehat{F}(\vec{u}) - \widehat{F}(\vec{u}^{\,\mathrm{old}}) \le \vec{v}\cdot(\vec{u}-\vec{u}^{\,\mathrm{old}}) &= \sum_{l\in\mathcal{V}}(u_0^l - u_0^{l\,\mathrm{old}})v_0^l + \sum_{\nu=1}^m\sum_{k\in\mathcal{V}}(u_\nu^k - u_\nu^{k\,\mathrm{old}})v_\nu^k \\
&= \sum_{l\in\mathcal{V}}\sum_{\nu=1}^m q_\nu \sum_{k\in\mathcal{V}}\frac{|V_\varepsilon^l\cap V_\nu^k|}{|V_\nu^k|}(u_\nu^k - u_\nu^{k\,\mathrm{old}})v_0^l + \sum_{\nu=1}^m\sum_{k\in\mathcal{V}}(u_\nu^k - u_\nu^{k\,\mathrm{old}})v_\nu^k \\
&= \sum_{\nu=1}^m\sum_{k\in\mathcal{V}}(u_\nu^k - u_\nu^{k\,\mathrm{old}})\Big[v_\nu^k + q_\nu\sum_{l\in\mathcal{V}}\frac{|V_\varepsilon^l\cap V_\nu^k|}{|V_\nu^k|}v_0^l\Big] \\
&= \sum_{\nu=1}^m\sum_{k\in\mathcal{V}}(u_\nu^k - u_\nu^{k\,\mathrm{old}})\cdot\zeta_\nu^k.
\end{aligned}$$

Next, we insert the discrete continuity equations and obtain

$$\begin{aligned}
\widehat{F}(\vec{u}) - \widehat{F}(\vec{u}^{\,\mathrm{old}}) &\le h\sum_{\nu=1}^m\sum_{k\in\mathcal{V}}\Big(-\sum_{l\in\mathcal{V}}J_\nu^{kl}|\partial V_\nu^k\cap\partial V_\nu^l|\zeta_\nu^k + R_\nu^k\zeta_\nu^k\Big) \\
&= -h\sum_{\nu=1}^m\sum_{k,l\in\mathcal{V},\,l\le k}\overline{u}_\nu\, Z_\nu^{kl}\frac{(\zeta_\nu^l-\zeta_\nu^k)^2}{|x^l-x^k|}|\mathbf{S}_\nu n_\nu^{kl}|\partial V_\nu^k\cap\partial V_\nu^l| \\
&\quad + h\sum_{\nu=1}^m\sum_{k\in\mathcal{V}}R_\nu^k\zeta_\nu^k.
\end{aligned}$$

The last but one line containing the parts from drift-diffusion is non-positive, because of $Z_\nu^{kl} > 0$, since the functions g_ν are strictly monotonously increasing (see (53) and (A2)). The summand

$$\begin{aligned}
&\sum_{\nu=1}^m\sum_{k\in\mathcal{V}}R_\nu^k\zeta_\nu^k \\
&= \sum_{\nu=1}^m\sum_{k\in\mathcal{V}}\sum_{(\alpha,\beta)\in\mathcal{R}}(\beta_\nu-\alpha_\nu)\sum_{k_1\in\mathcal{V}}\cdots\sum_{k_{\nu-1}\in\mathcal{V}}\sum_{k_{\nu+1}\in\mathcal{V}}\cdots\sum_{k_m\in\mathcal{V}}R_{\alpha\beta}\big[\zeta_1^{k_1},\dots,\zeta_{\nu-1}^{k_{\nu-1}},\zeta_\nu^k,\zeta_{\nu+1}^{k_{\nu+1}},\dots,\zeta_m^{k_m}\big] \\
&\qquad\times|V_1^{k_1}\cap\dots\cap V_{\nu-1}^{k_{\nu-1}}\cap V_\nu^k\cap V_{\nu+1}^{k_{\nu+1}}\cap\dots\cap V_m^{k_m}|\zeta_\nu^k \\
&= \sum_{(\alpha,\beta)\in\mathcal{R}}\sum_{k_1\in\mathcal{V}}\cdots\sum_{k_m\in\mathcal{V}}R_{\alpha\beta}\big[\zeta_1^{k_1},\dots,\zeta_m^{k_m}\big]\sum_{\nu=1}^m(\beta_\nu-\alpha_\nu)\zeta_\nu^{k_\nu}\,|V_1^{k_1}\cap\dots\cap V_m^{k_m}|
\end{aligned}$$

is non-positive due to (55) and the monotonicity of the exponential function. Thus we arrive at $\widehat{F}(\vec{u}) \le \widehat{F}(\vec{u}^{\,\mathrm{old}})$ and our scheme is dissipative. $\square$

Remark 4.2 *Gajewski, Gärtner [5] use a Crank-Nicholson like time discretization to show the dissipativeness for a discrete scheme for a nonlocal phase segregation model. This is necessary due to the fact that the free energy functional in that model is not convex. In our convex situation we can apply an Euler backward scheme because we can exploit inequality* (56) *to proceed in the proof of Theorem 4.2.*

4.5 Remarks concerning heterostructures

We assume a 2D heterostructure, where in subregions the material parameters are constants and consider the following model problem. Let $\Omega \in \mathbb{R}^2$ be composed by two connected, bounded, nonempty polyhedral open subsets Ω^A and Ω^B with one common edge $\Gamma_H = \overline{\Omega^A} \cap \overline{\Omega^B}$, $\overline{\Omega} = \overline{\Omega^A} \cup \overline{\Omega^B}$. On Ω^I we have constant material parameters $\overline{u}^I_\nu$, $k^I_{\alpha\beta}$, $\mathbf{S}^I_\nu$, μ^{kI}_ν, Q^I_ν, $I = A, B$. Moreover, (see (3), (7)) we denote

$$\varphi^I_0 := \max_{\nu=0,\ldots,m} \arccos \frac{\min(\mu^{1I}_\nu, \mu^{2I}_\nu)}{\max(\mu^{1I}_\nu, \mu^{2I}_\nu)}.$$

According to (A3) and (A6) we have $\varphi^I_0 \in [0, \pi/2)$. We consider a grid $\{x^k : x^k \in \overline{\Omega},\ k = 1, \ldots, M\}$ which respects the interface Γ_H.

Lemma 4.2 *Let for all directly neighboring grid points x^k and x^m on the heterostructure interface Γ_H and all inner grid points $x^l \in \Omega^I$ the inequality*

$$\frac{|x^k - x^l|^2 + |x^m - x^l|^2 - |x^k - x^m|^2}{2|x^k - x^l||x^m - x^l|} \geq \sin \varphi^I_0$$

be fulfilled. Then all directly neighboring grid points on the interface Γ_H are directly neighboring in the metric induced by the anisotropy matrices $\mathbf{S}^I_\nu$, $\nu = 0, \ldots, m$, $I = A, B$, too.

Proof. We show the assertion for arbitrarily fixed I and ν and skip these indeces in the proof. Let x^k and x^m be directly neighboring grid points on Γ_H and let x^l be any inner grid point in Ω^I (cf. Fig. 1). We have to ensure that

$$d(x^k, \frac{x^k + x^m}{2}) \leq d(x^l, \frac{x^k + x^m}{2}), \quad d(x^m, \frac{x^k + x^m}{2}) \leq d(x^l, \frac{x^k + x^m}{2}).$$

We prove the first estimate (the second uses analogous arguments). The line $\{y : d(y, x^l) = d(y, x^k)\}$ (lightgray solid line in Fig. 1 with normal vector n^{kl}) arises by rotation of the midperpendicular to $x^k - x^l$ (lightgrey dashed line) by a vector φ with

$$\cos \varphi = \frac{(\mathbf{S}n^{kl}, n^{kl})}{|\mathbf{S}n^{kl}||n^{kl}|} \geq \frac{\min(\mu^1, \mu^2)}{\max(\mu^1, \mu^2)}.$$

Thus $|\varphi| \leq \varphi_0$ (see Remark 4.1, 2), too). If φ is negative, nothing more is to show. Otherwise we must guarantee that the angle γ in Fig. 1 is less or equal to $\pi/2 - \varphi_0$. Since

$$\gamma = \arccos \frac{|x^k - x^l|^2 + |x^m - x^l|^2 - |x^k - x^m|^2}{2|x^k - x^l||x^m - x^l|}$$

and the cos function is monotonously decreasing on $(0, \pi)$ this requirement is equivalent to

$$\frac{|x^k - x^l|^2 + |x^m - x^l|^2 - |x^k - x^m|^2}{2|x^k - x^l||x^m - x^l|} \geq \cos\left(\frac{\pi}{2} - \varphi_0\right) = \sin \varphi_0$$

which we formulated in the lemma. $\square$

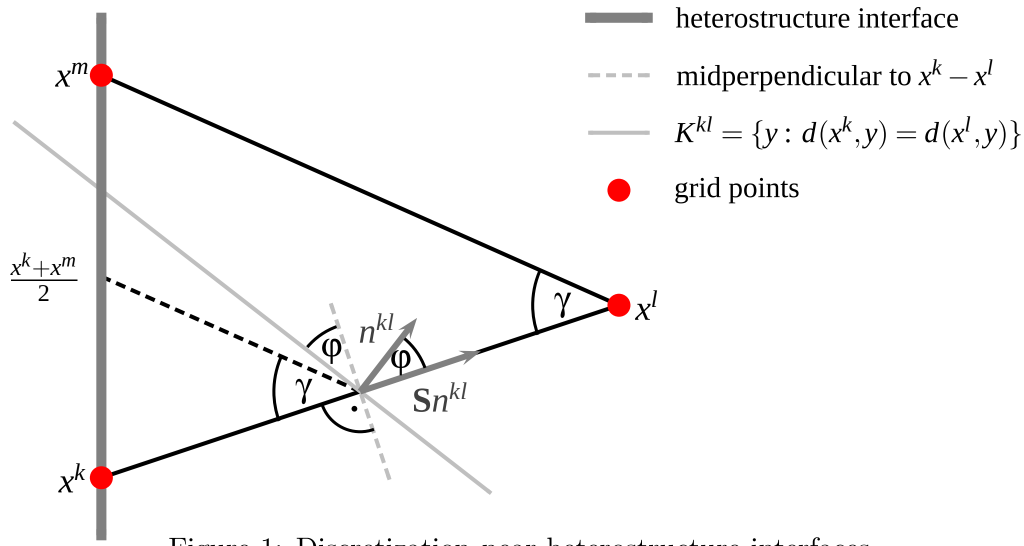

Figure 1: Discretization near heterostructure interfaces

Remark 4.3 *Let κ denote the quotient of the maximal distance of two directly neighboring grid points on the heterostructure interface Γ_H and of the minimal distance of inner grid points to the heterostructure interface Γ_H and let $\varphi_0^* := \max(\varphi_0^A, \varphi_0^B)$. Then the condition*

$$\kappa \leq \sqrt{2 - 2\sin\varphi_0^*} \tag{57}$$

is sufficient for the assertion of Lemma 4.2.

Remark 4.4 *The severe restriction* (57) *on the placement of vertices on and close to interfaces and boundaries allows to handle general heterostructures and boundary conditions. The described integration procedure can be applied independently on each Ω^I and the fluxes and potentials fulfill the continuity conditions.*
If $Q_\nu^I = Q^I$ holds, the restriction can be seriously relaxed, especially in cases of straight line interfaces. But still the largest eigenvalue ratio for each Ω^I defines a forbidden region for interior vertices around the interfaces or boundaries.

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