Weierstraß–Institut
für Angewandte Analysis und Stochastik
im Forschungsverbund Berlin e.V.

Preprint ISSN 0946 – 8633

Uniform exponential decay of the free energy for Voronoi finite volume discretized reaction-diffusion systems

Annegret Glitzky

submitted: 28th September 2009

Weierstrass Institute for
Applied Analysis and Stochastics
Mohrenstraße 39
10117 Berlin, Germany
E-Mail: glitzky@wias-berlin.de

Preprint No. 1443

Berlin 2009

2000 *Mathematics Subject Classification.* 35B40, 35K57, 35R05, 46E39, 65M12.

Key words and phrases. Reaction-diffusion systems, energy estimates, thermodynamic equilibria, asymptotic behaviour, time and space discretization, boundary conforming Delaunay grid, Voronoi finite volume scheme, discrete Sobolev-Poincaré inequality.

Edited by
Weierstraß–Institut für Angewandte Analysis und Stochastik (WIAS)
Mohrenstraße 39
D — 10117 Berlin
Germany

Fax: + 49 30 2044975
E-Mail: preprint@wias-berlin.de
World Wide Web: http://www.wias-berlin.de/

Abstract

Our focus are energy estimates for discretized reaction-diffusion systems for a finite number of species. We introduce a discretization scheme (Voronoi finite volume in space and fully implicit in time) which has the special property that it preserves the main features of the continuous systems, namely positivity, dissipativity and flux conservation.

For a class of Voronoi finite volume meshes we investigate thermodynamic equilibria and prove for solutions to the evolution system the monotone and exponential decay of the discrete free energy to its equilibrium value with a unified rate of decay for this class of discretizations. The fundamental idea is an estimate of the free energy by the dissipation rate which is proved indirectly by taking into account sequences of Voronoi finite volume meshes. Essential ingredient in that proof is a discrete Sobolev-Poincaré inequality.

1 Model equations, notation, and assumptions

Let $\Omega \subset \mathbb{R}^N$ be a bounded domain, $\Gamma := \partial\Omega$. We consider m species X_i with initial densities U_i. These species undergo chemical reactions and underly diffusion processes. We assume Boltzmann statistics giving the relation between the densities u_i of the species X_i and the corresponding chemical potentials v_i,

$$u_i = \overline{u}_i \mathrm{e}^{v_i}, \quad i = 1, \dots, m, \tag{1.1}$$

where the reference densities $\overline{u}_i$ may depend on the spatial position and express the possible heterogeneity of the system under consideration. For the fluxes j_i of the species X_i we make the ansatz

$$j_i = -\mu_i u_i \nabla v_i, \ i = 1, \dots, m, \tag{1.2}$$

with mobility coefficients μ_i. 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 form

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

According to the mass action law, 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, $a_i := \exp(v_i)$ is the chemical activity of X_i, and $a^\alpha := \prod_{i=1}^m a_i^{\alpha_i}$. The net production rate of species X_i corresponding to the reaction rates for all reactions taking place is

$$R_i := \sum_{(\alpha,\beta)\in\mathcal{R}} k_{\alpha\beta}(a^\alpha - a^\beta)(\beta_i - \alpha_i). \tag{1.3}$$

The m continuity equation can be written as follows:

$$\begin{aligned} &\frac{\partial u_i}{\partial t} + \nabla \cdot j_i = R_i \text{ in } \mathbb{R}_+ \times \Omega, \quad \nu \cdot j_i = 0 \text{ on } \mathbb{R}_+ \times \Gamma, \\ &u_i(0) = U_i \text{ in } \Omega, \quad i = 1, \dots, m. \end{aligned} \tag{1.4}$$

Problem (1.4) has been investigated in various papers, see e.g. [15], [5, 6, 12, 13, 14] for electrically charged species and [10] with different anisotropies for the different species. The papers [5, 6, 10, 12] deal with more general state equations. In [9] the limit case of partly fast kinetics is studied.

The aim of the present paper is to show that there are discretization schemes (Euler backward in time and Voronoi finite volume meshes in space) for problem (1.4) such that the discretized free energy along the discrete solutions decays exponentially to its equilibrium value. The essential new result in this paper is to prove a uniform decay rate for a class of meshes. In [8] we already proved dissipativeness of the scheme and established the finite dimensional estimates for a fixed given mesh.

To obtain the uniform estimates for a class of Voronoi finite volume meshes we have to translate the quantities from the finite dimensional discretized problems into expressions of functions being defined on Ω and being constant on Voronoi boxes of the corresponding meshes and we have to consider limits of such functions to find a contradiction in the indirect proof of a Poincaré like estimate of the free energy by the dissipation rate (see Theorem 3.2).

The paper is organized as follows. In Section 2 we give a weak formulation (P) of problem (1.4), formulate common assumptions and collect known results concerning energy estimates for (P). Section 3 is the heard of the paper. First, we introduce the space discretization by Voronoi finite volume meshes, and give some notation used in the finite volume context (Subsection 3.1). Subsection 3.2 contains the full discretization scheme (P$\mathcal{M}$) of the reaction-diffusion system (1.4). The finite dimensional discrete energy functionals are introduced in Subsection 3.3. In Subsection 3.4 we give the steady states of the discretized reaction-diffusion systems and discuss their relation to the steady state of (P). The most important results are proven in Subsection 3.5, namely the uniform estimate of the discretized free energy by the discretized dissipation rate (Theorem 3.2) and the exponential decay of the discretized free energy to its equilibrium value with a decay rate not depending on the mesh (Theorem 3.3). The paper ends with Section 4 where remarks and open questions are formulated.

2 Continuous reaction-diffusion systems

2.1 Weak formulation

In the whole paper we assume

(A1) Ω is an open, bounded Lipschitzian domain in $\mathbb{R}^N$, $N = 2, 3$, $\Gamma = \partial\Omega$;

$\mu_i,\ \overline{u}_i,\ U_i \in L^\infty_+(\Omega),\ \mu_i,\ \overline{u}_i \geq \delta > 0,\ \ q_i \in \mathbb{Z},\ \ i = 1, \ldots, m;$

$\mathcal{R} \subset \mathbb{Z}^m_+ \times \mathbb{Z}^m_+$ finite subset, $k_{\alpha\beta} \in L^\infty_+(\Omega),\ k_{\alpha\beta} \geq \delta > 0$ for all $(\alpha, \beta) \in \mathcal{R}$.

If $N = 3$ then $\max_{(\alpha,\beta)\in\mathcal{R}} \max\Big\{ \sum_{i=1}^m \alpha_i, \sum_{i=1}^m \beta_i \Big\} \leq 3$.

To give a weak formulation of the equations (1.4) we introduce the spaces

$$V := H^1(\Omega; \mathbb{R}^m),\ \ W := V \cap L^\infty(\Omega, \mathbb{R}^m),$$

and the stoichiometric subspaces

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

In addition to (A1) we assume that we are given an initial value $U \in V^*$ such that

$$\text{(A2)} \qquad U = \big(U_1, \dots, U_m\big), \; \sum_{i=1}^m \lambda_i \langle U_i, 1\rangle > 0 \text{ if } \lambda = (\lambda_1, \dots, \lambda_m) \in \mathcal{S}_+^\perp \backslash \{0\}.$$

V^* denotes the space dual to V, and 1 means the constant function on Ω taking the value 1. Note that (A2) is satisfied if the initial value of the vector function $u := (u_1, \dots, u_m)$ fulfills $U_i \geq 0$, $U_i \neq 0$, $i = 1, \dots, m$. We define operators A, $E : W \to V^*$,

$$\begin{aligned} \langle Av, \widehat{v}\rangle &:= \int_\Omega \sum_{i=1}^m \mu_i \overline{u}_i \mathrm{e}^{v_i}\, \nabla v_i \cdot \nabla \widehat{v}_i \,\mathrm{d}x + \int_\Omega \sum_{(\alpha,\beta)\in\mathcal{R}} k_{\alpha\beta}(a^\alpha - a^\beta)(\alpha - \beta)\cdot \widehat{v}\,\mathrm{d}x, \\ Ev &:= \big(\overline{u}_1 \mathrm{e}^{v_1}, \dots, \overline{u}_m \mathrm{e}^{v_m}\big), \quad v \in W,\, \widehat{v} \in V. \end{aligned} \tag{2.1}$$

A weak formulation of the transient problem (1.4) with (1.1), (1.2), (1.3) is given by

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

2.2 Summary of results on energy estimates for the continuous problem

We collect results on energy estimates which should be carried over from the continuous problem to a time and space discretized version of (P) in a unified manner for a class of Voronoi finite volume meshes.

The dissipation rate corresponding to Problem (P), $D(v) := \langle Av, v\rangle$, $v \in W$, has the form

$$D(v) = \int_\Omega \sum_{i=1}^m \mu_i \overline{u}_i \mathrm{e}^{v_i}\; \nabla v_i \cdot \nabla v_i \,\mathrm{d}x + \int_\Omega \sum_{(\alpha,\beta)\in\mathcal{R}} k_{\alpha\beta}(\mathrm{e}^{v\cdot\alpha} - \mathrm{e}^{v\cdot\beta})(\alpha - \beta)\cdot v\,\mathrm{d}x \geq 0.$$

For $u \in V^* \cap L^2_+(\Omega)^m$ the free energy $F(u)$ is given by

$$F(u) = \int_\Omega \sum_{i=1}^m \Big\{ u_i \Big(\ln \frac{u_i}{\overline{u}_i} - 1\Big) + \overline{u}_i \Big\} \,\mathrm{d}x.$$

Moreover, we define the subspaces

$$\begin{aligned} \mathcal{U} &:= \{u \in V^* :\; (\langle u_1, 1\rangle, \dots, \langle u_m, 1\rangle) \in \mathcal{S}\}, \\ \mathcal{U}^\perp &:= \Big\{ v \in V : \langle u, v\rangle = 0 \quad \forall u \in \mathcal{U} \Big\} = \Big\{ v \in V : \nabla v = 0,\, v \in \mathcal{S}^\perp \Big\}. \end{aligned} \tag{2.2}$$

If (u, v) is a solution to (P) 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 $u^* \in U + \mathcal{U}$.

Theorem 2.1 *We assume* (A1) *and* (A2). *Then there exists a unique solution* (u^*, v^*) *to*

$$Av^* = 0, \quad u^* = Ev^*, \quad u^* \in U + \mathcal{U}, \quad v^* \in W. \tag{S}$$

We define the set

$$\mathcal{A} := \Big\{ a \in \mathbb{R}^m_+ : \ a^\alpha = a^\beta \text{ for all } (\alpha, \beta) \in \mathcal{R}, \ u \in \mathcal{U} + U, \text{ where } u_i = \overline{u}_i a_i, \ i = 1, \dots, m \Big\}$$

and assume

(A3) $\quad \mathcal{A} \cap \partial\mathbb{R}^m_+ = \emptyset$.

Remark 2.1 We assume (A1). On the one hand, if (u, v) is a solution to (S) then $a = (\mathrm{e}^{v_1}, \dots, \mathrm{e}^{v_m}) \in \mathcal{A}$. On the other hand, if $a \in \mathcal{A}$ and $a_i > 0$, $i = 1, \dots, m$, then (u, v) defined by $v_i := \ln a_i$, $u_i := \overline{u}_i \mathrm{e}^{v_i}$, $i = 1, \dots, m$, is a steady state of (P), that is a solution to (S). If in addition (A2) and (A3) are fulfilled then $\mathcal{A} = \{a^*\}$.

Theorem 2.2 *Let* (A1) – (A3) *be fulfilled, let* (u, v) *be a solution to Problem* (P)*, and let* (u^*, v^*) *be the thermodynamic equilibrium* (*cf. Theorem 2.1*)*. Then the free energy along the solution* (u, v) *decays monotonously and there exists a* $\lambda > 0$ *such that*

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

The proof of Theorem 2.2 is mainly based on a Poincaré type inequality which gives an estimate of the free energy by the dissipation rate as formulated in Lemma 2.1.

Lemma 2.1 *Let* (A1) – (A3) *be fulfilled. Moreover, let* (u^*, v^*) *be the thermodynamic equilibrium according to Theorem 2.1. Then for every* $\rho > 0$ *there exists a constant* $c_\rho > 0$ *such that*

$$F(u) - F(u^*) \le c_\rho D(v) \tag{2.3}$$

for all $v \in \mathcal{N}_\rho = \{v \in W : \ F(Ev) - F(u^*) \le \rho, \ u = Ev \in U + \mathcal{U}\}$.

For these results we refer to [10, Theorem 2.1, Theorem 3.1, Theorem 3.2], [15, Theorem 1, Theorem 2, Corollary of Theorem 2] and [5, Theorem 7.1, Theorem 7.2].

3 Discretized reaction-diffusion systems

3.1 Space discretization

Although we work with boundary conforming Delaunay grids where the Voronoi boxes are the dual grid our notation is basically taken from [1, 3] since we need results provided there for more general finite volume meshes. Have in mind that Voronoi meshes are admissible finite volume meshes in the sense of [3, Definition 9.1] (see [3, Example 9.2]).

Let Ω be an open, bounded, polyhedral subset of $\mathbb{R}^N$. A Voronoi mesh of Ω denoted by $\mathcal{M} = (\mathcal{P}, \mathcal{T}, \mathcal{E})$ is formed by a family of grid points $\mathcal{P}$ in $\overline{\Omega}$, a family $\mathcal{T}$ of Voronoi control volumes and a family of parts of hyperplanes in $\mathbb{R}^N$ denoted by $\mathcal{E}$ (which represent the faces of the Voronoi boxes). For Voronoi meshes we use the following notation.

Let M denote the number of grid points, $M = \#\mathcal{P}$. For each grid point of the set $\{x_K \in \mathcal{P}\}$ the control volume K of the Voronoi mesh belonging to the point x_K is defined by

$$K = \{x \in \Omega : |x - x_K| < |x - x_L| \quad \forall x_L \in \mathcal{P},\ x_L \neq x_K\}, \quad K \in \mathcal{T}.$$

mes(K) denotes the measure of Voronoi box $K \in \mathcal{T}$. The mesh size of $\mathcal{M}$ is defined by

$$\mathrm{size}(\mathcal{M}) = \sup_{K \in \mathcal{T}} \mathrm{diam}(K).$$

For K, $L \in \mathcal{T}$ with $K \neq L$ either the $(N-1)$ dimensional Lebesgue measure of $\overline{K} \cap \overline{L}$ is zero or $\overline{K} \cap \overline{L} = \overline{\sigma}$ for some $\sigma \in \mathcal{E}$. The symbol $\sigma = K|L$ denotes the Voronoi surface between K and L. We introduce the following subsets of $\mathcal{E}$. The set of interior Voronoi surfaces is denoted by $\mathcal{E}_{int}$. Additionally, for every $K \in \mathcal{T}$ we call $\mathcal{E}_K$ the subset of $\mathcal{E}$ such that $\partial K = \overline{K} \setminus K = \cup_{\sigma \in \mathcal{E}_K} \overline{\sigma}$. Then $\mathcal{E} = \cup_{K \in \mathcal{T}} \mathcal{E}_K$.

Moreover, for $\sigma \in \mathcal{E}$ we denote by m_σ the $(N-1)$ dimensional Lebesgue measure of the Voronoi surface σ. For $\sigma = K|L \in \mathcal{E}_{int}$ let d_σ be the Euclidean distance of x_K and x_L, see Figure 1, too.

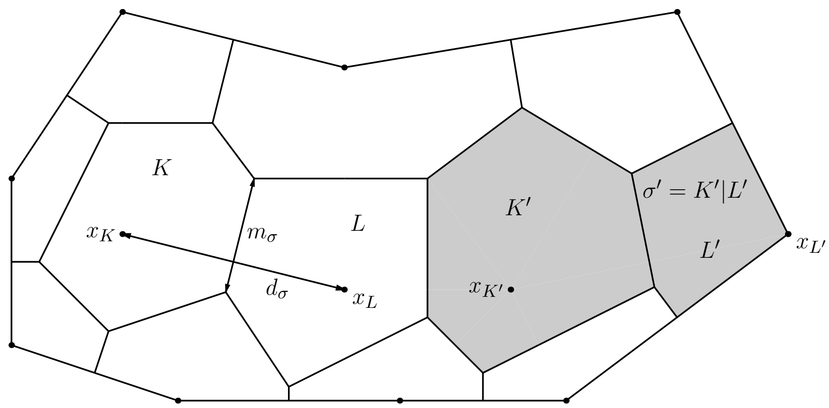

Figure 1: Notion of Voronoi finite volume meshes $\mathcal{M} = (\mathcal{P}, \mathcal{T}, \mathcal{E})$.

Definition. Let Ω be an open, bounded, polyhedral subset of $\mathbb{R}^N$ and $\mathcal{M}$ a Voronoi finite volume mesh.

1. $X(\mathcal{M})$ denotes the set of functions from Ω to $\mathbb{R}$ which are constant on each Voronoi box of the mesh. For $\underline{w} \in X(\mathcal{M})$ the value at the Voronoi box $K \in \mathcal{T}$ is denoted by w_K.

2. For $\underline{w} \in X(\mathcal{M})$ the discrete H^1-seminorm of $\underline{w}$, $|\underline{w}|_{1,\mathcal{M}}$, is defined by

$$|\underline{w}|^2_{1,\mathcal{M}} = \sum_{\sigma \in \mathcal{E}_{int}} \frac{m_\sigma}{d_\sigma} (D_\sigma \underline{w})^2, \quad D_\sigma \underline{w} = |w_K - w_L|, \tag{3.1}$$

where $\sigma = K|L$ and w_K is the value of $\underline{w}$ on the Voronoi box K.

For our considerations in Section 3 we use the additional assumptions

(A4) Let $\Omega \subset \mathbb{R}^N$ be a polyhedral domain and let $\overline{\Omega} = \cup_{I\in\mathcal{I}}\overline{\Omega}_I$ be a finite disjoint union of subdomains such that the discontinuities of $\overline{u}_i$, $i = 1, \dots, m$, coincide with subdomain boundaries. Let the over all $(N-1)$ dimensional measure of all internal subdomain boundaries be bounded by θ. There exists some $\gamma \in (0, 1]$ such that $\overline{u}_i \in \mathcal{C}^{0,\gamma}(\Omega_I) := \{w|_{\Omega_I}, w \in C^{0,\gamma}(\mathbb{R}^N)\}$, $i = 1, \dots, m$, $I \in \mathcal{I}$.

If $N = 3$ then $\max_{(\alpha,\beta)\in\mathcal{R}} \max\Big\{\sum_{i=1}^m \alpha_i, \sum_{i=1}^m \beta_i\Big\} < 3$.

Let $\mathcal{M}$ be a Voronoi finite volume mesh of Ω, where $\mathcal{P}$ is a boundary conforming Delaunay grid (see [2, 4]).

We introduce coefficient functions being constant on the Voronoi boxes $K \in \mathcal{T}$,

$$\mu_{iK} = \tfrac{1}{\mathrm{mes}(K)} \int_K \mu_i(x)\,\mathrm{d}x, \quad \overline{u}_{iK} = \tfrac{1}{\mathrm{mes}(K)} \int_K \overline{u}_i(x)\,\mathrm{d}x, \quad k_{\alpha\beta K} = \tfrac{1}{\mathrm{mes}(K)} \int_K k_{\alpha\beta}(x)\,\mathrm{d}x.$$

Note that the corresponding piecewise constant functions $\underline{\mu_i}$, $\underline{\overline{u}_i}$, $\underline{k_{\alpha\beta}}$ can be estimated from above and below by the upper and lower bounds of μ_i, $\overline{u}_i$, $k_{\alpha\beta}$, respectively.

For $K \in \mathcal{T}$ we denote by $u_i^{(K)}$ the mass of the i-th species in K and by u_{iK} the constant density on K, $u_{iK} = \frac{u_i^{(K)}}{\mathrm{mes}(K)}$. Associated to the grid points we have chemical potentials v_{iK}, $i = 1, \dots, m$. The discrete version of the state equations (1.1) then is

$$u_i^{(K)} = \overline{u}_{iK}\mathrm{e}^{v_{iK}}\mathrm{mes}(K), \quad k \in \mathcal{T}, \ i = 1, \dots, m. \tag{3.2}$$

To vectors characterized by lower indices, w_K, $K \in \mathcal{T}$, we associate a function $\underline{w} \in X(\mathcal{M})$.

3.2 A discretization scheme for reaction-diffusion systems

(A5) Let $\mathcal{Z} = \{t_0, t_1, \dots, t_n, \dots\}$ be a partition of $\mathbb{R}_+$ with $t_0 = 0$, $t_n \in \mathbb{R}_+$,

$t_{n-1} < t_n$, $n \in \mathbb{N}$, $t_n \to +\infty$ as $n \to \infty$, $\overline{h} := \sup_{n\in\mathbb{N}}(t_n - t_{n-1}) < \infty$.

We introduce the discrete initial values

$$U_i^{(K)} := \int_K U_i\,\mathrm{d}x, \quad K \in \mathcal{T}, \ i = 1, \dots, m.$$

The space discrete version of the continuity equations (1.4) is obtained by testing the corresponding equations with the characteristic function of K and using Gauss theorem for the divergence terms. We obtain the following discrete reaction-diffusion system (P$\mathcal{M}$) where the time discretization is done fully implicitly

$$\left.\begin{aligned}
\frac{u_i^{(K)}(t_n) - u_i^{(K)}(t_{n-1})}{t_n - t_{n-1}} - \sum_{\sigma=K|L\in\mathcal{E}_K} Y_i^\sigma\, Z_i^\sigma(t_n)\big(v_{iL}(t_n) - v_{iK}(t_n)\big)\frac{m_\sigma}{d_\sigma} &= R_i^{(K)}(t_n),\\
u_i^{(K)}(t_n) = \overline{u}_{iK}\,\mathrm{e}^{v_{iK}(t_n)}\mathrm{mes}(K), \quad i = 1, \dots, m, \ n &\geq 1,\\
u_i^{(K)}(0) = U_i^{(K)}, \quad i = 1, \dots, m, \quad K &\in \mathcal{T},
\end{aligned}\right\} \quad (\mathrm{P}\mathcal{M})$$

where the source terms $R_i^{(K)}$ have to be calculated by

$$R_i^{(K)}(t_n) = \sum_{\alpha,\beta\in\mathcal{R}} (\beta_i - \alpha_i) k_{\alpha\beta K} \Big(\exp\Big\{ \sum_{j=1}^m \alpha_j v_{jK}(t_n) \Big\} - \exp\Big\{ \sum_{j=1}^m \beta_j v_{jK}(t_n) \Big\} \Big) \mathrm{mes}(K),$$

$$Z_i^\sigma(t_n) = \frac{\mathrm{e}^{v_{iK}(t_n)} + \mathrm{e}^{v_{iL}(t_n)}}{2}, \quad \sigma = K|L,$$

and Y_i^σ represents some mean value of $\mu_i \overline{u}_i$ associated to the face $\sigma = K|L$ which is symmetric in K and L and fulfills $\operatorname{ess\,inf}_{x\in\Omega} \mu_i \ \operatorname{ess\,inf}_{x\in\Omega} \overline{u}_i \le Y_i^\sigma \le \|\mu_i\|_{L^\infty} \|\overline{u}_i\|_{L^\infty}$. Possible choices are e.g.

$$Y_i^\sigma = \frac{\mu_{iK} + \mu_{iL}}{2} \, \frac{\overline{u}_{iK} + \overline{u}_{iL}}{2} \ \text{ or } \ Y_i^\sigma = \frac{1}{\mathrm{mes}(K) + \mathrm{mes}(L)} \int_{K\cup L} \mu_i(x) \overline{u}_i(x) \, \mathrm{d}x, \ \sigma = K|L.$$

3.3 Discrete energy functionals

We use the notation

$$\begin{aligned} &\vec{u} = (\vec{u}_1, \dots, \vec{u}_m), \quad \vec{v} = (\vec{v}_1, \dots, \vec{v}_m), \quad \vec{u}_i = \big(u_i^{(K)}\big)_{K\in\mathcal{T}}, \quad \vec{v}_i = \big(v_{iK}\big)_{K\in\mathcal{T}}, \\ &\vec{U} = (\vec{U}_1, \dots, \vec{U}_m), \quad \vec{U}_i = \big(U_i^{(K)}\big)_{K\in\mathcal{T}}, \quad i = 1, \dots, m. \end{aligned}$$

The discrete dissipation rate $\widehat{D} : \mathbb{R}^{Mm} \to \mathbb{R}$ corresponding to Problem (P$\mathcal{M}$) is given by

$$\begin{aligned} \widehat{D}(\vec{v}) = &\sum_{i=1}^m \sum_{\sigma = K|L \in \mathcal{E}_{int}} Y_i^\sigma \, Z_i^\sigma |v_{iK} - v_{iL}|^2 \frac{m_\sigma}{d_\sigma} \\ &+ \sum_{(\alpha,\beta)\in\mathcal{R}} \sum_{K\in\mathcal{T}} k_{\alpha\beta K} \Big(\exp\Big\{ \sum_{j=1}^m \alpha_j v_{jK} \Big\} - \exp\Big\{ \sum_{j=1}^m \beta_j v_{jK} \Big\} \Big) \sum_{i=1}^m (\alpha_i - \beta_i) v_{iK} \mathrm{mes}(K). \end{aligned}$$

Due to (A1) and the monotonicity of the exponential function this discrete dissipation rate is nonnegative, $\widehat{D}(\vec{v}) \ge 0$ for all $\vec{v} \in \mathbb{R}^{Mm}$.

Next, we define as a discrete version of E (cf. (2.1)) the operator $\widehat{E} \colon \mathbb{R}^{Mm} \to \mathbb{R}^{Mm}$,

$$\widehat{E}\vec{v} = \Big(\big(\overline{u}_{iK} \mathrm{e}^{v_{iK}} \mathrm{mes}(K) \big)_{K\in\mathcal{T}} \Big)_{i=1,\dots,m}.$$

The equation $\vec{u} = \widehat{E}\vec{v}$ then contains the discretized state equations (3.2). Corresponding to $\widehat{E}$, we obtain the discrete potential $\widehat{G} \colon \mathbb{R}^{Mm} \to \mathbb{R}$, and introduce the discrete free energy $\widehat{F}$ as the conjugate functional,

$$\widehat{G}(\vec{v}) = \sum_{i=1}^m \sum_{K\in\mathcal{T}} \overline{u}_{iK} (\mathrm{e}^{v_{iK}} - 1) \mathrm{mes}(K), \quad \widehat{F}(\vec{u}) = \sup_{\vec{v}\in\mathbb{R}^{Mm}} \big\{ \langle \vec{u}, \vec{v} \rangle_{\mathbb{R}^{Mm}} - \widehat{G}(\vec{v}) \big\}. \tag{3.3}$$

Then $\widehat{F} : \mathbb{R}^{Mm} \to \overline{\mathbb{R}}$ is convex and lower semicontinuous. $\widehat{F}$ is differentiable in arguments $\vec{u}$, where $u_i^{(K)} > 0$, $K \in \mathcal{T}$, $i = 1, \dots, m$. 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 $\vec{u} = \widehat{E}\vec{v}$, $\vec{v} \in \mathbb{R}^{Mm}$ the inequality

$$\widehat{F}(\vec{w}) - \widehat{F}(\vec{u}) \ge \langle \vec{w} - \vec{u}, \widehat{F}'(\vec{u}) \rangle_{\mathbb{R}^{Mm}} \quad \forall \vec{w} \in \mathbb{R}^{Mm}, \tag{3.4}$$

which guarantees that the (Euler backward in time) discretization scheme (P$\mathcal{M}$) is dissipative. Moreover, for $\vec{u} = \widehat{E}\vec{v}$ we calculate

$$\widehat{F}(\vec{u}) = \langle \widehat{E}\vec{v}, \vec{v}\rangle_{\mathbb{R}^{Mm}} - \widehat{G}(\vec{v}) = \sum_{i=1}^{m} \sum_{K\in\mathcal{T}} \Big(u_i^{(K)} v_{iK} - u_i^{(K)} + \overline{u}_{iK}\mathrm{mes}(K)\Big).$$

3.4 Steady states for the discretized reaction-diffusion system

In analogy to the continuous situation (see (2.2)) we define

$$\widehat{\mathcal{U}} = \Big\{ \vec{u} \in \mathbb{R}^{Mm} : \big(\sum_{K\in\mathcal{T}} u_1^{(K)}, \dots, \sum_{K\in\mathcal{T}} u_m^{(K)} \big) \in \mathcal{S} \Big\}$$

and $\widehat{\mathcal{U}}^\perp = \{\vec{v} \in \mathbb{R}^{Mm} : \langle \vec{u}, \vec{v}\rangle_{\mathbb{R}^{Mm}} = 0 \;\; \forall \vec{u} \in \widehat{\mathcal{U}}\}$ which can be characterized by

$$\widehat{\mathcal{U}}^\perp = \Big\{ \vec{v} \in \mathbb{R}^{Mm} : v_{iK} = v_i,\ K \in \mathcal{T},\ i = 1, \dots, m,\ (v_1, \dots, v_m) \in \mathcal{S}^\perp \Big\}.$$

Any solution $(\vec{u}, \vec{v})$ to the discretized Problem (P$\mathcal{M}$) fulfills

$$\vec{u}(t_n) - \vec{U} \in \widehat{\mathcal{U}} \quad \forall n \in \mathbb{N}. \tag{3.5}$$

This invariance property follows by [8, Lemma 3.2]. Using the corresponding $\underline{u}(t_n) \in X(\mathcal{M})$, the initial value U and the set $\mathcal{U}$ from the continuous setting we rewrite (3.5) as

$$\underline{u}(t_n) - U \in \mathcal{U} \quad \forall n \in \mathbb{N}.$$

We are looking for steady states $(\vec{u}, \vec{v})$ of the discretized Problem (P$\mathcal{M}$) fulfilling the property $\vec{u} - \vec{U} \in \widehat{\mathcal{U}}$, and consider the problem

$$\left.\begin{aligned} \sum_{\sigma=K|L\in\mathcal{E}_K} Y_i^\sigma\, Z_i^\sigma \big(v_{iL} - v_{iK}\big) \frac{m_\sigma}{d_\sigma} = R_i^{(K)},\ K \in \mathcal{T},\ i = 1, \dots, m,& \\ \vec{u} = \widehat{E}\vec{v}, \quad \vec{u} - \vec{U} \in \widehat{\mathcal{U}}.& \end{aligned}\right\} \tag{S$\mathcal{M}$}$$

Theorem 3.1 *We assume* (A1), (A2) *and* (A4). *Then there is a unique solution* $(\vec{u}^*, \vec{v}^*)$ *to Problem* (S$\mathcal{M}$). *This solution satisfies* $\vec{v}^* \in \widehat{\mathcal{U}}^\perp$.

Proof. The proof is a special case of [8, Theorem 3.1] if no anisotropies and no charged species are taken into account. Have in mind that our coefficients $\overline{u}_i$, μ_i, $k_{\alpha\beta}$ now are L^∞ functions in contrast to (A9) in [8]. But an inspection of the proof shows the validity of the result for this situation, too. □

Corollary 3.1 *We assume* (A1) – (A4). *Let the pair* (u^*, v^*) *be the solution to* (S) (*cf. Theorem 2.1*) *and* $(\vec{u}^*, \vec{v}^*)$ *the solution to* (S$\mathcal{M}$) (*see Theorem 3.1*). *Then the corresponding piecewise constant functions* $\underline{u}^*$, $\underline{v}^*$ *and* $\underline{a}^*$ *are related to the thermodynamic equilibrium quantities of the continuous problem* u^*, v^* *and* a^* *by*

$$\underline{u}_i^* = \frac{\overline{\underline{u}_i}}{\overline{u}_i} u_i^*, \quad i = 1, \dots, m, \quad \underline{v}^* = v^*, \quad \underline{a}^* = a^*.$$

Proof. If $(\vec{u}^*, \vec{v}^*)$ is the solution to (S$\mathcal{M}$) then $\widehat{D}(\vec{v}^*) = 0$ which guarantees that $v_{iK}^* = v_i^\circ$, $K \in \mathcal{T}$, $(v_1^\circ, \ldots, v_m^\circ) \in \mathcal{S}^\perp$. The discrete chemical activities $\underline{a}_i^* := \mathrm{e}^{v_i^\circ} = \mathrm{e}^{v_{iK}^*} = a_{iK}^*$, $K \in \mathcal{T}$, then fulfill

$$\underline{a}^* \in \mathbb{R}_+^m, \quad (\underline{a}^*)^\alpha = (\underline{a}^*)^\beta \quad \forall (\alpha, \beta) \in \mathcal{R}.$$

Since $\vec{u}^* = \widehat{E}\vec{v}^* \in \vec{U} + \widehat{\mathcal{U}}$ we find that $\underline{u}^* - U \in \mathcal{U}$. Thus, for all $\eta \in \mathcal{S}^\perp$

$$0 = \sum_{i=1}^m \int_\Omega (\underline{u}_i^* - U_i)\eta_i \,\mathrm{d}x = \sum_{i=1}^m \int_\Omega (\underline{a}_i^* \underline{\overline{u}}_i - U_i)\eta_i \,\mathrm{d}x = \sum_{i=1}^m \int_\Omega (\underline{a}_i^* \overline{u}_i - U_i)\eta_i \,\mathrm{d}x.$$

Therefore the constructed $\underline{a}^*$ belongs to the set $\mathcal{A}$. According to (A3) and Remark 2.1 we have $\mathcal{A} = \{a^*\}$. This ensures that $\underline{a}^* = a^*$. And thus $\underline{v}^* = v^*$ and $\underline{u}_i^* = \frac{\underline{\overline{u}}_i}{\overline{u}_i} u_i^*$. $\square$

3.5 Energy estimates for the discretized reaction-diffusion system

We start with some upper and lower estimates of $\widehat{F}(\vec{u}) - \widehat{F}(\vec{u}^*)$ by means of the piecewise constant functions $\underline{u}$ and $\underline{u}^*$.

Lemma 3.1 *We assume* (A1), (A2) *and* (A4). *Let* $\vec{u} = \widehat{E}\vec{v} \in \vec{U} + \widehat{\mathcal{U}}$ *and let* $(\vec{u}^*, \vec{v}^*)$ *be the discrete thermodynamic equilibrium according to Theorem 3.1. Moreover, let* $\underline{u}$, $\underline{u}^* \in X(\mathcal{M})$ *be the piecewise constant functions corresponding to* $\vec{u}$ *and* $\vec{u}^*$. *Then there exist constants* c_1, $c_2 > 0$ *not depending on the mesh* $\mathcal{M}$ *such that*

$$c_1 \sum_{i=1}^m \|\sqrt{\underline{u}_i} - \sqrt{\underline{u}_i^*}\|_{L^2}^2 \le \widehat{F}(\vec{u}) - \widehat{F}(\vec{u}^*) \le c_2 \sum_{i=1}^m \|\underline{u}_i - \underline{u}_i^*\|_{L^2}^2.$$

Proof. Using the assumptions of the lemma, $\langle \vec{u} - \vec{u}^*, \vec{v}^* \rangle_{\mathbb{R}^{Mm}} = 0$ and (3.3) we evaluate

$$\begin{aligned}
\widehat{F}(\vec{u}) - \widehat{F}(\vec{u}^*) &= \langle \vec{u}, \vec{v} \rangle_{\mathbb{R}^{Mm}} - \widehat{G}(\vec{v}) - \langle \vec{u}^*, \vec{v}^* \rangle_{\mathbb{R}^{Mm}} + \widehat{G}(\vec{v}^*) \\
&= \langle \vec{u}, \vec{v} - \vec{v}^* \rangle_{\mathbb{R}^{Mm}} - \widehat{G}(\vec{v}) + \widehat{G}(\vec{v}^*) \\
&= \sum_{i=1}^m \sum_{K \in \mathcal{T}} \overline{u}_{iK} \mathrm{mes}(K) \Big(\mathrm{e}^{v_{iK}} (v_{iK} - v_{iK}^*) - \mathrm{e}^{v_{iK}} + \mathrm{e}^{v_{iK}^*} \Big) \\
&= \sum_{i=1}^m \int_\Omega \underline{\overline{u}}_i \Big(\mathrm{e}^{\underline{v}_i} (\underline{v}_i - \underline{v}_i^*) - \mathrm{e}^{\underline{v}_i} + \mathrm{e}^{\underline{v}_i^*} \Big) \,\mathrm{d}x \\
&= \sum_{i=1}^m \int_\Omega \Big(\underline{u}_i \ln \frac{\underline{u}_i}{\underline{u}_i^*} - \underline{u}_i + \underline{u}_i^* \Big) \,\mathrm{d}x.
\end{aligned}$$

Using the estimates $x \ln \frac{x}{y} - x + y \ge (\sqrt{x} - \sqrt{y})^2$ and $x \ln \frac{x}{y} - x + y \le \frac{1}{y}(x - y)^2$ for x, $y > 0$ in the arguments $x = \underline{u}_i$, $y = \underline{u}_i^*$ and taking into account that $\underline{u}_i^* = \frac{\underline{\overline{u}}_i}{\overline{u}_i} u_i^*$, and that $\overline{u}_i$, $\underline{\overline{u}}_i$ are bounded (uniformly for all $\mathcal{M}$) we find the desired estimates. $\square$

Next, we want to prove a Poincaré type inequality (similar to Lemma 2.1 for the continuous case) which gives for the discretized situation an estimate of the free energy by the dissipation rate. This estimate is desired to be independent on the underlying mesh $\mathcal{M}$.

In [8, Theorem 3.2] we presented an indirect proof for one given mesh. But we could not show that the constant is universal for a certain class of meshes.

To establish this qualitative new result, we have to formulate some additional **assumptions on the geometry and the meshes**:

(A6) We assume that $\Omega \subset \mathbb{R}^N$ is star shaped with respect to some ball $B(y_0, R)$.

Let ϱ be the function $\varrho : \mathbb{R}^N \to [0, 1]$,

$$\varrho(y) = \begin{cases} \exp\left\{ -\frac{R^2}{R^2 - |y-y_0|^2}\right\} & \text{if } |y - y_0| < R, \\ 0 & \text{if } |y - y_0| \geq R. \end{cases}$$

We introduce piecewise constant approximations $\varrho^{\mathcal{M}} \in X(\mathcal{M})$ by

$$\varrho_K^{\mathcal{M}}(x) = \min_{y \in \overline{K}} \varrho(y) \quad \text{for } x \in K. \tag{3.6}$$

Let κ_0, κ_1, $\kappa_2 \in \mathbb{R}$ with $0 < \kappa_0 < \int_{\mathbb{R}^N} \varrho(x)\,\mathrm{d}x$, $\kappa_1 > 0$ and $\kappa_2 \geq \frac{1}{2}$ be given. For all finite volume meshes $\mathcal{M}$ under consideration we additionally suppose the following two properties:

(A7) Let $\mathcal{M} = (\mathcal{P}, \mathcal{T}, \mathcal{E})$ be a Voronoi finite volume mesh of Ω with $\int_\Omega \varrho^{\mathcal{M}}(x)\,\mathrm{d}x \geq \kappa_0$ and with the property that $\mathcal{E}_K \cap \mathcal{E}_{ext} \neq \emptyset$ implies $x_K \in \partial\Omega$.

(A8) The geometric weights fulfill

$0 < \mathrm{diam}(\sigma) \leq \kappa_1\, d_\sigma$ for all $\sigma \in \mathcal{E}_{\mathrm{int}}$ and

$\max\limits_{\sigma \in \mathcal{E}_K \cap \mathcal{E}_{int}} |x_K - x_\sigma| \leq \kappa_2 \min\limits_{\sigma \in \mathcal{E}_K \cap \mathcal{E}_{int}} d_\sigma$ for all $x_K \in \mathcal{P}$.

These additional assumptions guarantee the validity of a discrete Sobolev-Poincaré inequality for functions with arbitrary boundary values (see [11, Theorem 2.2]) which is needed in the proof of Theorem 3.2.

Theorem 3.2 *We assume* (A1) – (A4) *and* (A6) *and consider Voronoi finite volume meshes $\mathcal{M}$ fulfilling* (A7) *and* (A8). *Let for $\mathcal{M}$ the pair $(\vec{u}^*, \vec{v}^*)$ be the thermodynamic equilibrium of* (P$\mathcal{M}$) *according to Theorem 3.1. Then for every $\rho > 0$ there exists a mesh size $\kappa_\rho > 0$ and a constant $c_\rho > 0$ such that for all these Voronoi finite volume meshes $\mathcal{M}$ with size$(\mathcal{M}) \leq \kappa_\rho$ and all $\vec{v} \in \widehat{\mathcal{N}}_\rho := \left\{ \vec{v} \in \mathbb{R}^{Mm} : \ \widehat{F}(\widehat{E}\vec{v}) - \widehat{F}(\vec{u}^*) \leq \rho, \ \vec{u} = \widehat{E}\vec{v} \in \vec{U} + \widehat{\mathcal{U}} \right\}$ the inequality*

$$\widehat{F}(\vec{u}) - \widehat{F}(\vec{u}^*) \leq c_\rho \widehat{D}(\vec{v}) \tag{3.7}$$

is fulfilled.

Proof. In this proof we denote by c (possibly different) positive constants depending only on the data but not depending on the mesh.

1. Let $\rho > 0$ be arbitrarily given. For $\vec{v} \in \mathbb{R}^{Mm}$ we can estimate

$$\widehat{D}(\vec{v}) \geq c \sum_{i=1}^{m} \sum_{\sigma \in \mathcal{E}_{int}} Z_i^\sigma |D_\sigma \underline{v}_i|^2 \frac{m_\sigma}{d_\sigma} + c \sum_{(\alpha,\beta)\in\mathcal{R}} \int_\Omega \Big(\exp\Big\{ \sum_{i=1}^{m} \underline{v}_i \frac{\alpha_i}{2} \Big\} - \exp\Big\{ \sum_{i=1}^{m} \underline{v}_i \frac{\beta_i}{2} \Big\} \Big)^2 \mathrm{d}x$$
$$=: D_1(\vec{v}).$$

Here we used (A1), (A4), (3.1) and the inequality $(x-y)\ln\frac{x}{y} \geq |\sqrt{x}-\sqrt{y}|^2$ for $x, y > 0$. Therefore it suffices to prove the inequality

$$\widehat{F}(\vec{u}) - \widehat{F}(\vec{u}^*) \leq C D_1(\vec{v}) \quad \forall \vec{v} \in \widehat{\mathcal{N}}_\rho \tag{3.8}$$

with some constant $C > 0$ not depending on the mesh $\mathcal{M}$ (if $\mathrm{size}(\mathcal{M}) \leq \kappa_\rho$).

2. If (3.8) would be false, then we would find a sequence of Voronoi finite volume meshes $\mathcal{M}_n$ with $\mathrm{size}(\mathcal{M}_n) \to 0$ and corresponding $\vec{v}_n \in \widehat{\mathcal{N}}_\rho$, $\vec{u}_n = \widehat{E}\vec{v}_n \in \vec{U} + \widehat{\mathcal{U}}$, $n \in \mathbb{N}$, such that

$$\widehat{F}(\vec{u}_n) - \widehat{F}(\vec{u}_n^*) = C_n D_1(\vec{v}_n) > 0, \tag{3.9}$$

and $\lim_{n\to\infty} C_n = +\infty$. Clearly, for each $\mathcal{M}_n$ we have to use the corresponding quantities M, $\vec{U}$, $\widehat{E}$, $\widehat{F}$, D_1,... and sets $\mathcal{E}_{int}$, $\widehat{\mathcal{U}}$, $\widehat{\mathcal{N}}_\rho$. But we don't write them with an index $\mathcal{M}_n$. Let $a_{niK} = \mathrm{e}^{v_{niK}}$, $K \in \mathcal{T}_n$. By $\underline{u}_{ni}$, $\underline{v}_{ni}$, $\underline{a}_{ni} \in X(\mathcal{M}_n)$, $i = 1, \ldots, m$, we denote the corresponding piecewise constant functions.

Since

$$\|\sqrt{\underline{a}_{ni}} - \sqrt{\underline{a}_{ni}^*}\|_{L^2}^2 \leq c \|\sqrt{\underline{u}_{ni}} - \sqrt{\underline{u}_{ni}^*}\|_{L^2}^2 \leq \frac{c}{c_1}\big(\widehat{F}(\vec{u}_n) - \widehat{F}(\vec{u}_n^*)\big) \leq c(\rho) \tag{3.10}$$

by assumption and Lemma 3.1 and because of $\underline{a}_{ni}^* = a_i^*$ (see Corollary 3.1) we find

$$\|\sqrt{\underline{a}_{ni}}\|_{L^2} \leq c(\rho), \quad i = 1, \ldots, m, \text{ for all } n \tag{3.11}$$

with a suitable constant c depending only on ρ.

3. We write for $\sigma = K|L \in \mathcal{E}_{int}$, $i = 1, \ldots, m$,

$$(\sqrt{a_{niK}} - \sqrt{a_{niL}})^2 = \Big(\frac{\mathrm{e}^{\frac{v_{niK}}{2}} - \mathrm{e}^{\frac{v_{niL}}{2}}}{v_{niK} - v_{niL}} \Big)^2 \frac{2}{\mathrm{e}^{v_{niK}} + \mathrm{e}^{v_{niL}}} \quad Z_i^\sigma\, |D_\sigma \underline{v}_{ni}|^2.$$

Using the generalized mean value theorem we estimate

$$\Big(\frac{\mathrm{e}^{\frac{v_{niK}}{2}} - \mathrm{e}^{\frac{v_{niL}}{2}}}{v_{niK} - v_{niL}} \Big)^2 \frac{2}{\mathrm{e}^{v_{niK}} + \mathrm{e}^{v_{niL}}} \leq \frac{1}{4} \mathrm{e}^{2\max\{\frac{v_{niK}}{2}, \frac{v_{niL}}{2}\}} \frac{2}{\mathrm{e}^{\max\{v_{niK}, v_{niL}\}}} = \frac{1}{2}.$$

Therefore we conclude that

$$\sum_{i=1}^{m} |\sqrt{\underline{a}_{ni}}|_{1,\mathcal{M}_n}^2 = \sum_{i=1}^{m} \sum_{\sigma \in \mathcal{E}_{int}} |D_\sigma \sqrt{\underline{a}_{ni}}|^2 \frac{m_\sigma}{d_\sigma} \leq c D_1(\vec{v}_n) \to 0.$$

Applying the discrete Poincaré inequality for functions with general boundary values (see [7, Lemma 4.2] or [11, Theorem A.1]) we find for the functions $\sqrt{\underline{a}_{ni}} \in X(\mathcal{M}_n)$ that

$$\sqrt{\underline{a}_{ni}} - m_\Omega(\sqrt{\underline{a}_{ni}}) \to 0 \quad \text{in} \quad L^2(\Omega) \quad \text{where} \quad m_\Omega(\sqrt{\underline{a}_{ni}}) := \frac{1}{\mathrm{mes}(\Omega)} \int_\Omega \sqrt{\underline{a}_{ni}}\, \mathrm{d}x,$$

$i = 1, \ldots, m$.

Moreover, applying to the function $\sqrt{\underline{a}_{ni}} \in X(\mathcal{M}_n)$ the discrete Sobolev-Poincaré inequality (see [11, Theorem 2.2, Corollary 2.1]) we obtain that

$$\|\sqrt{\underline{a}_{ni}} - m_\Omega(\sqrt{\underline{a}_{ni}})\|_{L^q} \leq c_q |\sqrt{\underline{a}_{ni}}|_{1,\mathcal{M}_n} \to 0 \tag{3.12}$$

with a constant $c_q > 0$ not depending on $\mathcal{M}_n$ for $q \in [1, \infty)$ if $N = 2$ and for $q \in [1, 6)$ if $N = 3$.

Since $m_\Omega(\sqrt{\underline{a}_{ni}}) \operatorname{mes}(\Omega) = \|\sqrt{\underline{a}_{ni}}\|_{L^1} \leq c\|\sqrt{\underline{a}_{ni}}\|_{L^2} \leq c(\rho)$ by (3.11) for all $\mathcal{M}_n$ we find (for a subsequence, and we restrict our further investigations to this subsequence) $m_\Omega(\sqrt{\underline{a}_{ni}}) \to \sqrt{\widehat{a}_i}$ in $\mathbb{R}$. Using that

$$|\sqrt{\underline{a}_{ni}} - \sqrt{\widehat{a}_i}| \leq |\sqrt{\underline{a}_{ni}} - m_\Omega(\sqrt{\underline{a}_{ni}})| + |m_\Omega(\sqrt{\underline{a}_{ni}}) - \sqrt{\widehat{a}_i}|$$

we conclude that

$$\sqrt{\underline{a}_{ni}} \to \sqrt{\widehat{a}_i} \quad \text{in} \quad L^q(\Omega), \quad i = 1, \ldots, m, \tag{3.13}$$

for $q \in [1, \infty)$ if $N = 2$ and for $q \in [1, 6)$ if $N = 3$. From

$$\underline{a}_{ni} - \widehat{a}_i = (\sqrt{\underline{a}_{ni}} - \sqrt{\widehat{a}_i})(\sqrt{\underline{a}_{ni}} + \sqrt{\widehat{a}_i}) = (\sqrt{\underline{a}_{ni}} - \sqrt{\widehat{a}_i})^2 + 2\sqrt{\widehat{a}_i}(\sqrt{\underline{a}_{ni}} - \sqrt{\widehat{a}_i})$$

we find that

$$\|\underline{a}_{ni} - \widehat{a}_i\|_{L^2} \leq \|\sqrt{\underline{a}_{ni}} - \sqrt{\widehat{a}_i}\|_{L^4}^2 + 2\sqrt{\widehat{a}_i}\|\sqrt{\underline{a}_{ni}} - \sqrt{\widehat{a}_i}\|_{L^2} \to 0. \tag{3.14}$$

Moreover, taking into account the restriction of the order of the reactions if $N = 3$ (see (A4)) and (3.13) we have for $(\alpha, \beta) \in \mathcal{R}$

$$\int_\Omega \Big(\prod_{i=1}^m (\underline{a}_{ni})^{\alpha_i/2} - \prod_{i=1}^m (\underline{a}_{ni})^{\beta_i/2}\Big)^2 \mathrm{d}x \to \int_\Omega \Big(\prod_{i=1}^m \widehat{a}_i^{\alpha_i/2} - \prod_{i=1}^m \widehat{a}_i^{\beta_i/2}\Big)^2 \mathrm{d}x.$$

Because of

$$0 \leq \int_\Omega \Big(\prod_{i=1}^m (\underline{a}_{ni})^{\alpha_i/2} - \prod_{i=1}^m (\underline{a}_{ni})^{\beta_i/2}\Big)^2 \mathrm{d}x \leq c D_1(\vec{v}_n) \to 0$$

we have for $\widehat{a} := (\widehat{a}_1, \ldots, \widehat{a}_m)$ necessarily that

$$\widehat{a}^\alpha = \widehat{a}^\beta \quad \forall (\alpha, \beta) \in \mathcal{R}. \tag{3.15}$$

4. For $y \in K$ where $K \in \mathcal{T}_n$ with $K \subset \Omega_I$ for some $I \in \mathcal{I}$ we estimate by (A4)

$$\begin{aligned} |\overline{\underline{u}}_{ni}(y) - \overline{u}_i(y)| &\leq \frac{1}{\operatorname{mes}(K)} \int_K |\overline{u}_i(x) - \overline{u}_i(y)| \,\mathrm{d}x \leq \frac{c}{\operatorname{mes}(K)} \int_K |x - y|^\gamma \,\mathrm{d}x \\ &\leq c \operatorname{size}(\mathcal{M}_n)^\gamma. \end{aligned}$$

For $y \in K$ with $\operatorname{mes}(K \cap \Omega_I) \neq 0$ and $\operatorname{mes}(K \cap \Omega_J) \neq 0$ for some $I \neq J$ we estimate $|\overline{\underline{u}}_{ni}(y) - \overline{u}_i(y)|$ by 2 times the $L^\infty(\Omega)$-bound of $\overline{u}_i$ (see (A1)). For each n the measure of the set

$$\{y \in \Omega : \, y \in K \in \mathcal{T}_n \text{ with } \operatorname{mes}(K \cap \Omega_I) \neq 0, \ \operatorname{mes}(K \cap \Omega_J) \neq 0, \ I \neq J \text{ for some } I, J \in \mathcal{I}\}$$

can be estimated by $2\theta\text{size}(\mathcal{M}_n)$, where θ is a bound for the over all $(N-1)$ dimensional measure of the internal subdomain boundaries (see (A4)). Since $\text{size}(\mathcal{M}_n) \to 0$ for $n \to \infty$ we conclude by the arguments of Step 4 that

$$\|\underline{\overline{u}}_{ni} - \overline{u}_i\|_{L^2} \le c\ \text{size}(\mathcal{M}_n)^\gamma + c\theta\ \text{size}(\mathcal{M}_n) \to 0 \quad (n \to \infty). \tag{3.16}$$

We introduce

$$\widehat{u}_i := \overline{u}_i\,\widehat{a}_i, \quad i = 1, \dots, m, \tag{3.17}$$

and estimate by (3.14) and (3.16)

$$\begin{aligned}\|\underline{u}_{ni} - \widehat{u}_i\|_{L^2} &= \|\underline{a}_{ni}\underline{\overline{u}}_{ni} - \widehat{a}_i\overline{u}_i\|_{L^2} \\ &\le \|\underline{a}_{ni} - \widehat{a}_i\|_{L^2}\|\underline{\overline{u}}_{ni}\|_{L^\infty} + \widehat{a}_i\|\underline{\overline{u}}_{ni} - \overline{u}_i\|_{L^2} \to 0 \quad (n \to \infty).\end{aligned}$$

5. We set $\widehat{u} := (\widehat{u}_1, \dots, \widehat{u}_m)$. Because of $\vec{u}_n - \vec{U} \in \widehat{\mathcal{U}}$ we obtain $\underline{u}_n - U \in \mathcal{U}$. And the convergence $\underline{u}_{ni} \to \widehat{u}_i$ in $L^2(\Omega)$, $i = 1, \dots, m$, from Step 4 gives $\widehat{u} - U \in \mathcal{U}$. Thus, together with (3.15) we find $\widehat{a} \in \mathcal{A}$, and according to (A3) and Remark 2.1 we obtain that $\widehat{a} = a^*$. By the definition of $\widehat{u}$ this yields $\widehat{u} = u^*$.

6. Because of Lemma 3.1, $\underline{u}^*_{ni} = \frac{\underline{\overline{u}}_{ni}}{\overline{u}_i} u^*_i$ (see Corollary 3.1) and due to the convergences $\underline{u}_{ni} \to u^*_i$ in $L^2(\Omega)$ and (3.16) we have

$$\begin{aligned}\lambda_n^2 := \widehat{F}(\vec{u}_n) - \widehat{F}(\vec{u}^*_n) &\le c_2 \sum_{i=1}^m \|\underline{u}_{ni} - \underline{u}^*_{ni}\|^2_{L^2} \\ &\le 2c_2 \sum_{i=1}^m \Big(\|\underline{u}_{ni} - u^*_i\|^2_{L^2} + \|u^*_i - \underline{u}^*_{ni}\|^2_{L^2}\Big) \\ &\le 2c_2 \sum_{i=1}^m \Big(\|\underline{u}_{ni} - u^*_i\|^2_{L^2} + \|\frac{u^*_i}{\overline{u}_i}\|^2_{L^\infty}\|\overline{u}_i - \underline{\overline{u}}_{ni}\|^2_{L^2}\Big) \to 0 \text{ as } n \to \infty.\end{aligned} \tag{3.18}$$

Additionally (according to (3.9)) we find

$$\frac{1}{C_n} = \frac{1}{\lambda_n^2} D_1(\vec{v}_n) \to 0 \text{ as } n \to \infty. \tag{3.19}$$

7. For all n we introduce

$$\underline{y}_{ni} := \frac{1}{\lambda_n}(\underline{u}_{ni} - \underline{u}^*_{ni}) \in X(\mathcal{M}_n), \quad \underline{b}_{ni} := \frac{1}{\lambda_n}\Big(\sqrt{\frac{\underline{a}_{ni}}{\widehat{a}_i}} - 1\Big) \in X(\mathcal{M}_n), \quad i = 1, \dots, m.$$

The relation

$$\big(b_{niK} - b_{niL}\big)^2 = \left(\frac{\sqrt{\frac{a_{niK}}{\widehat{a}_i}} - \sqrt{\frac{a_{niL}}{\widehat{a}_i}}}{v_{niK} - v_{niL}}\right)^2 \frac{2}{\mathrm{e}^{v_{niK}} + \mathrm{e}^{v_{niL}}}\ Z_i^{K|L}\frac{(v_{niK} - v_{niL})^2}{\lambda_n^2}$$

and the estimate

$$\left(\frac{\sqrt{\frac{a_{niK}}{\widehat{a}_i}} - \sqrt{\frac{a_{niL}}{\widehat{a}_i}}}{v_{niK} - v_{niL}}\right)^2 \frac{2}{\mathrm{e}^{v_{niK}} + \mathrm{e}^{v_{niL}}} \le \frac{1}{\widehat{a}_i}\left(\frac{\sqrt{a_{niK}} - \sqrt{a_{niL}}}{v_{niK} - v_{niL}}\right)^2 \frac{2}{\mathrm{e}^{v_{niK}} + \mathrm{e}^{v_{niL}}} \le \frac{1}{2\widehat{a}_i}$$

(compare Step 3, too) guarantee that

$$\sum_{i=1}^{m}|\underline{b}_{ni}|^2_{1,\mathcal{M}_n}=\sum_{i=1}^{m}\sum_{\sigma\in\mathcal{E}_{int}}|D_\sigma\underline{b}_{ni}|^2\frac{m_\sigma}{d_\sigma}\le c\frac{D_1(\vec{v}_n)}{\lambda_n^2}\to 0.$$

Applying to the function $\underline{b}_{ni}\in X(\mathcal{M}_n)$ the discrete Sobolev-Poincaré inequality [11, Theorem 2.2 and Corollary 2.1] we obtain that

$$\|\underline{b}_{ni}-m_\Omega(\underline{b}_{ni})\|_{L^q}\le c_q|\underline{b}_{ni}|_{1,\mathcal{M}_n}\to 0,\quad i=1,\dots,m, \tag{3.20}$$

with $c_q>0$ not depending on $\mathcal{M}_n$ for $q\in[1,\infty)$ if $N=2$ and for $q\in[1,6)$ if $N=3$.
Using $\widehat{a}_i=a_i^*=\underline{a}_{ni}^*$, (3.10) and (3.18) we obtain

$$\begin{aligned}|m_\Omega(\underline{b}_{ni})|\,\mathrm{mes}(\Omega)&\le\frac{1}{\lambda_n\sqrt{\widehat{a}_i}}\int_\Omega|\sqrt{\underline{a}_{ni}}-\sqrt{\widehat{a}_i}|\,\mathrm{d}x\le\frac{1}{\lambda_n\sqrt{a_i^*}}\|\sqrt{\underline{a}_{ni}}-\sqrt{\underline{a}_{ni}^*}\|_{L^1}\\&\le\frac{c}{\lambda_n}\|\sqrt{\underline{a}_{ni}}-\sqrt{\underline{a}_{ni}^*}\|_{L^2}\le\frac{c}{\lambda_n}(\widehat{F}(\vec{u}_n)-\widehat{F}(\vec{u}_n^*))^{1/2}\le\frac{c}{\lambda_n}\lambda_n=c\end{aligned}$$

for all $\mathcal{M}_n$. Thus we find (for a subsequence) $m_\Omega(\underline{b}_{ni})\to\widehat{b}_i$ in $\mathbb{R}$. By

$$|\underline{b}_{ni}-\widehat{b}_i|\le|\underline{b}_{ni}-m_\Omega(\underline{b}_{ni})|+|m_\Omega(\underline{b}_{ni})-\widehat{b}_i|$$

we conclude that

$$\underline{b}_{ni}\to\widehat{b}_i\quad\text{in}\quad L^q(\Omega),\quad i=1,\dots,m, \tag{3.21}$$

for $q\in[1,\infty)$ if $N=2$ and for $q\in[1,6)$ if $N=3$.
8. We define $\widehat{y}_i:=2\widehat{b}_iu_i^*=2\widehat{b}_i\widehat{a}_i\overline{u}_i$, $i=1,\dots,m$. Since

$$\begin{aligned}\underline{y}_{ni}&=\frac{1}{\lambda_n}(\underline{u}_{ni}-\underline{u}_{ni}^*)=\frac{\overline{\underline{u}}_{ni}}{\lambda_n}(\underline{a}_{ni}-\widehat{a}_i)=\frac{\overline{\underline{u}}_{ni}}{\lambda_n}(\sqrt{\underline{a}_{ni}}-\sqrt{\widehat{a}_i})(\sqrt{\underline{a}_{ni}}+\sqrt{\widehat{a}_i})\\&=\overline{\underline{u}}_{ni}\underline{b}_{ni}(\sqrt{\underline{a}_{ni}}+\sqrt{\widehat{a}_i})\sqrt{\widehat{a}_i}\end{aligned}$$

we can estimate

$$\begin{aligned}\|\underline{y}_{ni}-\widehat{y}_i\|_{L^2}&=\|\overline{\underline{u}}_{ni}\underline{b}_{ni}(\sqrt{\underline{a}_{ni}}+\sqrt{\widehat{a}_i})\sqrt{\widehat{a}_i}-2\widehat{b}_i\widehat{a}_i\overline{u}_i\|_{L^2}\\&\le\|\overline{\underline{u}}_{ni}(\sqrt{\underline{a}_{ni}}+\sqrt{\widehat{a}_i})\sqrt{\widehat{a}_i}\|_{L^4}\|\underline{b}_{ni}-\widehat{b}_i\|_{L^4}\\&+\|\widehat{b}_i\|_{L^\infty}\|\overline{\underline{u}}_{ni}(\sqrt{\underline{a}_{ni}}+\sqrt{\widehat{a}_i})\sqrt{\widehat{a}_i}-2\widehat{a}_i\overline{u}_i\|_{L^2}.\end{aligned}$$

According to $\|\underline{b}_{ni}-\widehat{b}_i\|_{L^4}\to 0$,

$$\|\overline{\underline{u}}_{ni}(\sqrt{\underline{a}_{ni}}+\sqrt{\widehat{a}_i})\sqrt{\widehat{a}_i}\|_{L^4}\le\|\overline{\underline{u}}_{ni}\|_{L^\infty}\sqrt{\widehat{a}_i}\Big(\|\sqrt{\underline{a}_{ni}}-\sqrt{\widehat{a}_i}\|_{L^4}+2\|\sqrt{\widehat{a}_i}\|_{L^4}\Big)\le c,$$

$$\|\overline{\underline{u}}_{ni}(\sqrt{\underline{a}_{ni}}+\sqrt{\widehat{a}_i})\sqrt{\widehat{a}_i}-2\widehat{a}_i\overline{u}_i\|_{L^2}\le 2\widehat{a}_i\|\overline{\underline{u}}_{ni}-\overline{u}_i\|_{L^2}+\|\overline{\underline{u}}_{ni}\|_{L^\infty}\sqrt{\widehat{a}_i}\|\sqrt{\underline{a}_{ni}}-\sqrt{\widehat{a}_i}\|_{L^2}\to 0$$

for $n\to\infty$ we conclude that

$$\underline{y}_{ni}\to\widehat{y}_i\text{ in }L^2(\Omega),\ i=1,\dots,m,\quad(n\to\infty).$$

9. In view of $\underline{u}_n - U \in \mathcal{U}$, $\underline{u}_n^* - U \in \mathcal{U}$ we have $\underline{y}_n = \frac{1}{\lambda_n}\{(\underline{u}_n - U) - (\underline{u}_n^* - U)\} \in \mathcal{U}$. Passing to the limit we find that $\widehat{y} \in \mathcal{U}$, thus

$$(\langle \widehat{y}_1, 1\rangle, \dots, \langle \widehat{y}_m, 1\rangle) \in \mathcal{S}. \tag{3.22}$$

By the definition of $\underline{b}_{ni}$ and $\widehat{a}$ we obtain for all $(\alpha, \beta) \in \mathcal{R}$,

$$\begin{aligned} \widehat{a}^{\,-\alpha}\left(\prod_{i=1}^m (\underline{a}_{ni})^{\alpha_i/2} - \prod_{i=1}^m (\underline{a}_{ni})^{\beta_i/2}\right)^2 &= \Big(\prod_{i=1}^m (\lambda_n \underline{b}_{ni} + 1)^{\alpha_i} - \prod_{i=1}^m (\lambda_n \underline{b}_{ni} + 1)^{\beta_i}\Big)^2 \\ &= \Big(\lambda_n \sum_{i=1}^m \underline{b}_{ni}(\alpha_i - \beta_i)\Big)^2 + Q_n, \end{aligned} \tag{3.23}$$

where

$$|Q_n| \le c\lambda_n^3 (|\underline{b}_n| + 1)^{p_0},$$
$$0 \le p_0 \le 2 \max_{(\alpha,\beta)\in\mathcal{R}} \max\Big\{\sum_{i=1}^m \alpha_i, \sum_{i=1}^m \beta_i\Big\}.$$

Assumption (A4) ensures $p_0 < 6$ if $N = 3$. Taking into account that $\lambda_n \to 0$ as $n \to \infty$ (see (3.18)), we find

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

This together with (3.19) and (3.23) gives

$$\lim_{n\to\infty} \int_\Omega \Big(\sum_{i=1}^m \underline{b}_{ni}(\alpha_i - \beta_i)\Big)^2 \,\mathrm{d}x = 0 \quad \forall (\alpha, \beta) \in \mathcal{R}.$$

Therefore,

$$\widehat{b} = (\widehat{b}_1, \dots, \widehat{b}_m) \in \mathcal{S}^\perp. \tag{3.24}$$

By the definition of $\widehat{y}_i$ in Step 8 and exploiting (3.22) and (3.24) we end up with

$$0 = \sum_{i=1}^m \langle \widehat{y}_i, \widehat{b}_i\rangle = 2\sum_{i=1}^m u_i^* \widehat{b}_i^2.$$

Thus $\widehat{b} = 0$, and $\widehat{y} = 0$.

10. By the definition of λ_n (see (3.18)) and Lemma 3.1 we find

$$1 = \frac{1}{\lambda_n^2}\Big(\widehat{F}(\vec{u}_n) - \widehat{F}(\vec{u}_n^*)\Big) \le c_2 \sum_{i=1}^m \|\underline{y}_{ni}\|_{L^2}^2 \to 0.$$

This contradiction shows that the assumption made at the beginning of Step 2 of the proof was wrong, i.e., (3.8) holds, and the proof is complete. □

Finally, we are able to prove the main result of the paper which concerns the (monotone and) uniform exponential decay of the free energy on solutions to the discretized Problems (P$\mathcal{M}$) for all Voronoi finite volume meshes fulfilling the properties (A4), (A7) and (A8).

Theorem 3.3 *We assume* (A1) – (A8). *For $\mathcal{M}$, let* $(\vec{u}^*, \vec{v}^*)$ *be the solution to* (S$\mathcal{M}$).
1. Then the (*fully implicit in time*) *discretization scheme* (P$\mathcal{M}$) *is dissipative, i.e. solutions* $(\vec{u}, \vec{v})$ *to* (P$\mathcal{M}$) *fulfill*

$$\widehat{F}(\vec{u}(t_{n_2})) \le \widehat{F}(\vec{u}(t_{n_1})) \le \widehat{F}(\vec{U}) \quad \textit{for all } t_{n_1} \le t_{n_2}.$$

2. Moreover, there exists a $\lambda > 0$ *not depending on the mesh* $\mathcal{M}$ *such that*

$$\widehat{F}(\vec{u}(t_n)) - \widehat{F}(\vec{u}^*) \le e^{-\lambda t_n}\big(\widehat{F}(\vec{U}) - \widehat{F}(\vec{u}^*)\big) \quad \forall n \ge 1.$$

Proof. 1. We use the steps 1 to 3 of the proof of [8, Theorem 3.3] and obtain that

$$\vec{u}(t_n) - \vec{U} \in \widehat{\mathcal{U}}, \quad n \ge 1,$$

and for $n_2 > n_1 \ge 0$ and $\lambda \ge 0$

$$\begin{aligned} &\mathrm{e}^{\lambda t_{n_2}}\Big(\widehat{F}(\vec{u}(t_{n_2})) - \widehat{F}(\vec{u}^*)\Big) - \mathrm{e}^{\lambda t_{n_1}}\Big(\widehat{F}(\vec{u}(t_{n_1})) - \widehat{F}(\vec{u}^*)\Big) \\ &\le \sum_{r=n_1+1}^{n_2} \mathrm{e}^{\lambda t_{r-1}}\,(t_r - t_{r-1})\Big\{\mathrm{e}^{\lambda \overline{h}}\lambda\big(\widehat{F}(\vec{u}(t_r)) - \widehat{F}(\vec{u}^*)\big) - \widehat{D}(\vec{v}(t_r))\Big\}. \end{aligned} \tag{3.25}$$

2. Since $\widehat{D}(\vec{v}) \ge 0$ for $\vec{v} \in \mathbb{R}^{Mm}$, we obtain by setting $\lambda = 0$ in (3.25) that

$$\widehat{F}(\vec{u}(t_{n_2})) \le \widehat{F}(\vec{u}(t_{n_1})) \le \widehat{F}(\vec{U}) \quad \forall n_2 \ge n_1 \ge 0.$$

3. Due to the proof of Lemma 3.1 and Corollary 3.1 we estimate

$$\begin{aligned} \widehat{F}(\vec{U}) - \widehat{F}(\vec{u}^*) &\le c_2 \sum_{i=1}^m \|\underline{U}_i - \underline{u}_i^*\|_{L^2}^2 \\ &\le c_2 \sum_{i=1}^m \max\{\|\underline{U}_i\|_{L^\infty}^2, \|\underline{u}_i^*\|_{L^\infty}^2\}\,\mathrm{mes}(\Omega) \\ &\le c_2 \sum_{i=1}^m \max\{\|U_i\|_{L^\infty}^2, \|u_i^*\|_{L^\infty}^2\}\,\mathrm{mes}(\Omega) =: \rho. \end{aligned}$$

The ρ defined in this way does not depend on the mesh $\mathcal{M}$ and we find $\widehat{F}(\vec{u}(t_r)) - \widehat{F}(\vec{u}^*) \le \rho$, $\vec{u}(t_r) = \widehat{E}\vec{v}(t_r) \in \vec{U} + \widehat{\mathcal{U}}$. This means $\vec{v}(t_r) \in \widehat{\mathcal{N}}_\rho$ for $r \ge 1$. Theorem 3.2 supplies a $c_\rho > 0$ such that (3.7) is fulfilled for all admissible meshes $\mathcal{M}$. Choosing now $\lambda > 0$ such that $\lambda \mathrm{e}^{\lambda \overline{h}} c_\rho < 1$ which again is independent of the mesh $\mathcal{M}$ (see (A5), too) and $n_1 = 0$, the estimate (3.25) proves the second part of the theorem. □

4 Remarks and open questions

Remark 4.1 The results of Theorem 3.2 and Theorem 3.3 remain valid if instead of (A6) and (A7), Ω is assumed to be a finite union of (suitably overlapping) star shaped domains, more precisely, if one supposes that

(A9) Ω is a finite union of open, polyhedral Ω_i, $i = 1, \ldots, J$, and there are $\widetilde{\delta} > 0$, $R > 0$, and points $z^i \in \Omega$ such that Ω_i as well as the set $\Omega_{i\widetilde{\delta}} := \Omega_i \cup \cup_{j \neq i}\{x \in \Omega_j : \operatorname{dist}(x, \Omega_i) < \widetilde{\delta}\}$ are star shaped with respect to the ball $B(z^i, R)$, $i = 1, \ldots, J$.

We introduce the functions

$$\varrho_i : \mathbb{R}^n \to [0,1], \quad \varrho_i(y) = \begin{cases} \exp\big\{-\frac{R^2}{R^2 - |y-z^i|^2}\big\} & \text{if } |y - z^i| < R, \\ 0 & \text{if } |y - z^i| \geq R, \end{cases}$$

and their piecewise constant approximations $\varrho_i^{\mathcal{M}} \in X(\mathcal{M})$. Concerning the mesh we assume

(A10) Let $\mathcal{M} = (\mathcal{P}, \mathcal{T}, \mathcal{E})$ be a Voronoi finite volume mesh of Ω with $\operatorname{size}(\mathcal{M}) < \widetilde{\delta}$, with $\int_\Omega \varrho_i^{\mathcal{M}}(x)\,\mathrm{d}x \geq \kappa_0$, $i = 1, \ldots, J$, and with the property that $\mathcal{E}_K \cap \mathcal{E}_{ext} \neq \emptyset$ implies $x_K \in \partial\Omega$.

Then the discrete Sobolev inequality holds true, too (see [11, Theorem 4.1]), and the arguments in the proof of Theorem 3.2 remain valid.

Remark 4.2 Let $N = 3$. In the continuous situation also for reactions of order three the results of Section 2 in Theorem 2.2 and Lemma 2.1 are true. For a fixed mesh we can prove a corresponding result for the resulting finite dimensional problem, too. But if we are interested in estimates which are independent of the mesh we needed in the indirect proof of Theorem 3.2 a discrete Sobolev-Poincaré inequality (for functions with general boundary conditions) for the discrete square roots of the chemical activities) for q equal to two times the maximal order of the reactions.

Note that the discrete Sobolev inequality for functions with zero boundaries values for $N = 3$ in the references [1, 3] allows for $q \in [1, 6]$. But the technique used there fails in the case of more general boundary values. In [11] Sobolev's integral representation is adapted to the discretized setting to prove the discretized Sobolev inequality for functions with general boundary values. And this method (also in the continuous case) gives only the result for $q \in [1, 6)$. Therefore our results Theorem 3.2 and Theorem 3.3 concern only reactions of order less than three. A unified decay rate of the free energy for problems involving reactions of order three in three space dimensions remains an open problem.

Remark 4.3 Let $N = 2$. If one takes into account charged species and problem (1.4) is extended by a Poisson equation for the electrostatic potential, for $N = 2$ the results of Theorem 2.2 and Lemma 2.1 remain true (see [10, Theorem 3.1, Theorem 3.2]). Here an essential tool in the indirect proof of [10, Theorem 3.1] is a boundedness result of Gröger [16] for the solution to elliptic boundary value problems with nonsmooth data and right hand side f fulfilling $f \ln f \in L^1(\Omega)$.

For a fixed mesh we can prove corresponding results for the finite dimensional problem, too (see [8, Theorem 3.2]). But if we are interested in uniform estimates with respect to a class of meshes a discrete variant of Grögers boundedness result would be needed. This, up to now is an open question, too.

References

1. Y. Coudière, T. Gallouët, and R. Herbin, *Discrete Sobolev Inequalities and L^p error estimates for approximate finite volume solutions of convection diffusion equations*, M2AN **35** (2001), 31–63.

2. B. Delaunay, *Sur la sphére*, Izvestia Akademii Nauk SSSR. Otd. Matem. Estestv. Nauk **7** (1934), 793–800.

3. R. Eymard, T. Gallouët, and R. Herbin, *The finite volume method*, Handbook of Numerical Analysis VII (Ph. Ciarlet and J. L. Lions, eds.), North Holland, 2000, pp. 723–1020.

4. P. Fleischmann, *Mesh generation for technology CAD in three dimensions*, Dissertation, Technische Universität Wien, 1999.

5. H. Gajewski and K. Gröger, *Reaction–diffusion processes of electrically charged species*, Math. Nachr. **177** (1996), 109–130.

6. H. Gajewski and I. V. Skrypnik, *Existence and uniqueness results for reaction-diffusion processes of electrically charged species*, Nonlinear Elliptic and Parabolic Problems (Zurich 2004), Progress in Nonlinear Differential Equations and Their Applications, vol. 64, Birkhäuser, Basel, 2005, pp. 151–188.

7. T. Gallouët, R. Herbin, and M. H. Vignal, *Error estimates on the approximate finite volume solution of convection diffusion equations with general boundary conditions*, SIAM J. Numer. Anal. **37** (2000), 1935–1972.

8. A. Glitzky, *Exponential decay of the free energy for discretized electro-reaction-diffusion systems*, Nonlinearity **21** (2008), 1989–2009.

9. ______, *Energy estimates for electro–reaction–diffusion systems with partly fast kinetics*, DCDS-A **25** (2009), 159–174.

10. A. Glitzky and K. Gärtner, *Energy estimates for continuous and discretized electro-reaction-diffusion systems*, Nonlinear Analysis **70** (2009), 788–805.

11. A. Glitzky and J. A. Griepentrog, *Discrete Sobolev-Poincaré inequalities for Voronoi finite volume approximations*, Preprint 1429, Weierstraß-Institut für Angewandte Analysis und Stochastik, Berlin, 2009.

12. A. Glitzky, K. Gröger, and R. Hünlich, *Free energy and dissipation rate for reaction diffusion processes of electrically charged species*, Applicable Analysis **60** (1996), 201–217.

13. A. Glitzky and R. Hünlich, *Energetic estimates and asymptotics for electro–reaction–diffusion systems*, Z. Angew. Math. Mech. **77** (1997), 823–832.

14. ______, *Global estimates and asymptotics for electro–reaction–diffusion systems in heterostructures*, Applicable Analysis **66** (1997), 205–226.

15. K. Gröger, *Free energy estimates and asymptotic behaviour of reaction–diffusion processes*, Preprint 20, Institut für Angewandte Analysis und Stochastik im Forschungsverbund Berlin e.V., Berlin, 1992.

16. ______, *Boundedness and continuity of solutions to second order elliptic boundary value problems*, Nonlinear Anal. **26** (1996), 539–549.