On energy estimates for electro–diffusion equations arising in semiconductor technology

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Abstract

The design of modern semiconductor devices requires the numerical simulation of basic fabrication steps. We investigate some electro–reaction–diffusion equations which describe the redistribution of charged dopants and point defects in semiconductor structures and which the simulations should be based on. Especially, we are interested in pair diffusion models. We present new results concerned with the existence of steady states and with the asymptotic behaviour of solutions which are obtained by estimates of the corresponding free energy and dissipation functionals.

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1. Introduction

In the design of modern semiconductor devices and in the development of their technology, device and process simulation programmes turned out to be very important tools. The simulation of modern technologies requires the continuous improvement of the underlying physical models and their analytical and numerical investigation.

One of the main steps in the preparing of semiconductor devices is the redistribution of dopants connected with or followed after the doping. In order to explain this process, different models have been developed. Of special interest are pair diffusion models (see e. g. [2,4,10]). They consist in a set of reaction–diffusion equations for charged dopants, point defects and dopant–defect pairs coupled with a Poisson equation for the electrostatic potential of the inner electric field. Besides of the mentioned species electrons and holes have to be taken into account. But we assume that their kinetics is very fast such that the Poisson equation is replaced by a nonlinear Poisson equation for the chemical potential of the electrons (see e. g. [7,10]).

Motivated by these considerations we investigate a rather general electro–reaction–diffusion system for m species X_i. We denote by ψ the chemical potential of the electrons, by $p_i(\psi)$ suitably chosen reference concentrations depending on ψ, and by

u_i, $a_i = u_i/p_i(\psi)$, $\zeta_i = \ln a_i$ the concentration, the electrochemical activity and the electrochemical potential of the i-th species where all variables are suitably scaled. We assume that the set $\{1,\dots,m\}$ is split into two parts $\{1,\dots,m\} = J \cup J'$, and formulate the initial boundary value problem which we are interested in as follows:

$$\begin{aligned}
\frac{\partial u_i}{\partial t} + \nabla\cdot j_i + \sum_{(\alpha,\beta)\in\mathcal{R}} (\alpha_i-\beta_i)\,R_{\alpha\beta} &= 0 \quad \text{on } (0,\infty)\times\Omega,\\
\nu\cdot j_i &= 0 \quad \text{on } (0,\infty)\times\partial\Omega,\ i\in J;\\
\frac{\partial u_i}{\partial t} + \sum_{(\alpha,\beta)\in\mathcal{R}} (\alpha_i-\beta_i)\,R_{\alpha\beta} &= 0 \quad \text{on } (0,\infty)\times\Omega,\quad i\in J';\\
-\nabla\cdot(\nabla\psi) + e(\psi) - \sum_{i=1}^m Q_i(\psi)u_i &= f \quad \text{on } (0,\infty)\times\Omega,\\
\nu\cdot\nabla\psi &= 0 \quad \text{on } (0,\infty)\times\partial\Omega;\\
u_i(0) &= U_i \quad \text{on } \Omega,\ i=1,\dots,m.
\end{aligned} \tag{1}$$

Here denote f a fixed charge density, $-e(\psi)$ the charge density of electrons and holes, and $Q_i(\psi) = -p_i'(\psi)/p_i(\psi)$ the charge of the i-th species depending on ψ, too. Only for species $i\in J$ there is a diffusive and convective transport given by the mass flux

$$j_i = -D_i(\psi)\Big[\nabla u_i + Q_i(\psi)\,u_i\nabla\psi\Big],\ i\in J.$$

But in all continuity equations occur source terms generated by a lot of mass action type reactions of the form

$$\alpha_1X_1+\ldots+\alpha_mX_m \rightleftharpoons \beta_1X_1+\ldots+\beta_mX_m,\ (\alpha,\beta)\in\mathcal{R},$$

where α, $\beta\in\mathbb{Z}_+^m$ are the vectors of stoichiometric coefficients of the reaction and $\mathcal{R}$ describes the set of all reactions under consideration. The corresponding reaction rate $R_{\alpha\beta}$ is given by

$$R_{\alpha\beta}(u,\psi) = k_{\alpha\beta}(\psi)\Big[\prod_{i=1}^m a_i^{\alpha_i} - \prod_{i=1}^m a_i^{\beta_i}\Big],\ u\in\mathbb{R}^m,\ \psi\in\mathbb{R},\ a_i = \frac{u_i}{p_i(\psi)},\ (\alpha,\beta)\in\mathcal{R}.$$

If each species has a constant charge then

$$p_i(\psi) = \overline{u}_i\,\mathrm{e}^{-q_i\psi},\ Q_i(\psi) = q_i,\ \overline{u}_i,\ q_i = \text{const},$$

and we arrive at a model which we have studied in great detail in [5,6,7,8] (for $J' = \emptyset$, but in a more general setting which is valid for heterostructures, too). There energy estimates, global existence and uniqueness of a solution and further qualitative properties of the solution have been established. For the pair diffusion model in [2,4] it holds

$$p_i(\psi) = \sum_{j\in J_i} \overline{u}_j\mathrm{e}^{-q_j\psi},\ Q_i(\psi) = \frac{\sum_{j\in J_i} q_j\overline{u}_j\mathrm{e}^{-q_j\psi}}{\sum_{j\in J_i} \overline{u}_j\mathrm{e}^{-q_j\psi}}. \tag{2}$$

It is the aim of this paper to show that the energy estimates are valid in this new situation, too. More precisely, we prove that under some assumptions concerning the initial value and the structure of the underlying reaction system (see assumptions (II), (III) later on) there exists a unique steady state to (1), and that the free energy along any solution to (1) remains bounded and decays monotonously and exponentially to its equilibrium value as t tends to infinity. From these assertions first global a priori estimates for solutions to (1) are obtained (see Corollary 1 – Corollary 3). We expect that based on these energy estimates further a priori estimates, and finally existence results could be derived. In this direction first results may be found in [12] (for $J' = \emptyset$ and for smooth data).

Notation. The notation of function spaces corresponds to that in [11]. By $\mathbb{Z}^m_+$, $\mathbb{R}^m_+$, L^p_+ we denote the cones of nonnegative elements. For the scalar product in $\mathbb{R}^m$ we use a centered dot. If $u \in \mathbb{R}^m$ then $u \geq 0$ ($u > 0$) means $u_i \geq 0\,\forall i$ ($u_i > 0\,\forall i$); $\sqrt{u}$ denotes the vector $\{\sqrt{u_i}\}_{i=1,\dots,m}$, and analogously $\ln u$, e^u are to be understood. If $u, v \in \mathbb{R}^m$ then $uv = \{u_i v_i\}_{i=1,\dots,m}$ and analogously for u/v. Finally, if $u \in \mathbb{R}^m_+$ and $\alpha \in \mathbb{Z}^m_+$ then u^α means the product $\prod_{i=1}^m u_i^{\alpha_i}$. In our estimates positive constants depending at most on the data of our problem are denoted by c.

2. Formulation of the problem

First we summarize the basic assumptions (I) which we assume to be fulfilled up to the end of the paper:

$$
\left.
\begin{aligned}
&\Omega \subset \mathbb{R}^2 \text{ bounded, Lipschitzian;}\\
&U \in L^\infty_+(\Omega, \mathbb{R}^m),\ f \in L^2(\Omega);\\
&e \in C^1(\mathbb{R}),\ |e(\psi)| \leq c\,\mathrm{e}^{c|\psi|},\ e'(\psi) \geq c > 0,\ \psi \in \mathbb{R};\\
&\mathcal{R} \subset \mathbb{Z}^m_+ \times \mathbb{Z}^m_+;\\
&k_{\alpha\beta} \in C(\mathbb{R}),\ k_{\alpha\beta}(\psi) > 0,\ \psi \in \mathbb{R},\ (\alpha, \beta) \in \mathcal{R};\\
&\{1, \dots, m\} = J \cup J',\ J \cap J' = \emptyset;\\
&Q_i \in C^1(\mathbb{R}),\ |Q_i(\psi)| \leq c,\ Q_i'(\psi) \leq 0,\\
&p_i(\psi) = p_{i0}\,\mathrm{e}^{-P_i(\psi)},\ p_{i0} > 0,\ P_i(\psi) = \int_0^\psi Q_i(s)\,\mathrm{d}s,\ \psi \in \mathbb{R},\ i \in J \cup J';\\
&\text{for } i \in J\ :\ D_i \in C(\mathbb{R}),\ D_i(\psi) > 0,\ \psi \in \mathbb{R};\\
&\text{for } i \in J' :\ \text{there is a reaction of the form } R_{\alpha\beta} = k_{\alpha\beta}(\psi)\Big[\prod_{j \in J} a_j^{\alpha_j} - a_i^2\Big].
\end{aligned}
\right\} \quad \text{(I)}
$$

The last two assumptions imply that there is a sufficiently high dissipation in the reaction–diffusion system, produced either by a diffusion–drift term ($i \in J$) or by a suitable quadratic reaction term ($i \in J'$). From (I) we easily find some further useful properties:

$$
\begin{aligned}
&p_i,\ P_i \in C^2(\mathbb{R}),\\
&p_i(\psi) > 0,\ p_i'(\psi) = -p_i(\psi)Q_i(\psi),\ p_i''(\psi) \ge 0,\ p_i(\psi), |p_i'(\psi)| \le c\,\mathrm{e}^{c|\psi|},\\
&|P_i'(\psi)| \le c,\ P_i''(\psi) \le 0,\ P_i(\psi) - Q_i(\psi)\psi \ge 0,\ \psi \in \mathbb{R},\ i = 1, \ldots, m;\\
&g \in C^1(\mathbb{R}) \text{ where } g(\psi) = e(\psi)\psi - \int_0^\psi e(s)\,\mathrm{d}s,\\
&g(\psi) \ge c\,\psi^2,\ g(\psi) \le c\,\mathrm{e}^{c|\psi|},\ \psi \in \mathbb{R};\\
&p_i(\psi),\ D_i(\psi),\ k_{\alpha\beta}(\psi) \ge c_R > 0,\ \psi \in \mathbb{R},\ |\psi| \le R.
\end{aligned}
\tag{3}
$$

Next we introduce the function spaces

$$
Y = L^2(\Omega, \mathbb{R}^m), \quad X = \{u \in Y\colon u_i \in H^1(\Omega)\ \forall\, i \in J\}
$$

and define the two operators

$$
A : (X \cap L^\infty(\Omega, \mathbb{R}^m)) \times (H^1(\Omega) \cap L^\infty(\Omega)) \to X^*, \quad E : H^1(\Omega) \times Y \to (H^1(\Omega))^*,
$$

$$
\begin{aligned}
\langle A(u,\psi), \overline{u}\rangle &= \int_\Omega \sum_{i\in J} D_i(\psi)\left[\nabla u_i + u_i Q_i(\psi)\nabla\psi\right]\cdot\nabla\overline{u}_i\,\mathrm{d}x\\
&+ \int_\Omega \sum_{(\alpha,\beta)\in\mathcal{R}} R_{\alpha\beta}(u,\psi)\sum_{i=1}^m(\alpha_i - \beta_i)\,\overline{u}_i\,\mathrm{d}x, \quad \overline{u} \in X,
\end{aligned}
$$

$$
\langle E(\psi,u), \overline{\psi}\rangle = \int_\Omega \left\{\nabla\psi\cdot\nabla\overline{\psi} + \left[e(\psi) - \sum_{i=1}^m u_i Q_i(\psi) - f\right]\overline{\psi}\right\}\mathrm{d}x, \quad \overline{\psi} \in H^1(\Omega).
$$

Because of (I) and of Trudinger's imbedding theorem [14] the operator $E(\cdot, u)$ turns out to be well defined on $H^1(\Omega)$ for every $u \in Y$. The precise formulation of the electro–diffusion system (1) now reads as follows:

$$
\begin{gathered}
u'(t) + A(u(t), \psi(t)) = 0, \quad E(\psi(t), u(t)) = 0, \quad u(t) \ge 0 \quad \text{f.a.a. } t > 0,\\
u(0) = U,\\
u \in L^2_{\mathrm{loc}}(\mathbb{R}_+, X) \cap L^\infty_{\mathrm{loc}}(\mathbb{R}_+, L^\infty(\Omega, \mathbb{R}^m)),\ u' \in L^2_{\mathrm{loc}}(\mathbb{R}_+, X^*),\\
\psi \in L^2_{\mathrm{loc}}(\mathbb{R}_+, H^1(\Omega)) \cap L^\infty_{\mathrm{loc}}(\mathbb{R}_+, L^\infty(\Omega)).
\end{gathered}
\tag{P}
$$

3. The nonlinear Poisson equation

Here we summarize some results concerned with the nonlinear Poisson equation.

Lemma 1. *For any $u \in Y_+ = L^2_+(\Omega, \mathbb{R}^m)$ there exists a unique solution ψ to $E(\psi, u) = 0$. Moreover, there are a positive constant c and a monotonously increasing function $d\colon \mathbb{R}_+ \to \mathbb{R}_+$ such that*

$$\|\psi - \overline{\psi}\|_{H^1} \le c\,\|u - \overline{u}\|_Y \quad \forall u, \overline{u} \in Y_+,\ E(\psi, u) = E(\overline{\psi}, \overline{u}) = 0,$$

$$\|\psi\|_{L^\infty} \le c\Big\{1 + \sum_{i=1}^m \|u_i \ln u_i\|_{L^1} + d(\|\psi\|_{H^1})\Big\} \quad \forall u \in Y_+,\ E(\psi, u) = 0.$$

Proof. Since for $u \in Y_+$ the operator $E(\cdot, u)$ is strongly monotone uniformly with respect to u as well as hemicontinuous, and since for $\psi \in H^1(\Omega)$ the operator $E(\psi, \cdot)$ is Lipschitz continuous uniformly with respect to ψ, the first and second assertions are obvious. The third assertion is a consequence of Gröger's regularity result [9] and of Trudinger's imbedding theorem [14]. ∎

Later on we are interested in a modified version of the Poisson equation which is obtained by setting $u = ap(\psi)$, $a \in \mathbb{R}^m$. We define $\widetilde{E} : H^1(\Omega) \times \mathbb{R}^m \to (H^1(\Omega))^*$ by

$$\langle \widetilde{E}(\psi, a), \overline{\psi}\rangle = \int_\Omega \Big\{\nabla\psi \cdot \nabla\overline{\psi} + \Big[e(\psi) + \sum_{i=1}^m a_i p_i'(\psi) - f\Big]\,\overline{\psi}\Big\}\,\mathrm{d}x, \quad \overline{\psi} \in H^1(\Omega).$$

Lemma 2. *For any $a \in \mathbb{R}^m_+$ there exists a unique solution ψ to $\widetilde{E}(\psi, a) = 0$. Moreover, for every $R > 0$ there is a positive constant $c(R)$ such that*

$$\|\psi\|_{H^1},\ \|\psi\|_{L^\infty} \le c(R) \quad \forall a \in R^m_+,\ \|a\|_{\mathbb{R}^m} \le R,\ \widetilde{E}(\psi, a) = 0,$$

$$\|\psi - \overline{\psi}\|_{H^1} \le c(R)\,\|a - \overline{a}\|_{\mathbb{R}^m}\ \forall a, \overline{a} \in \mathbb{R}^m_+,\ \|a\|_{\mathbb{R}^m}, \|\overline{a}\|_{\mathbb{R}^m} \le R,\ \widetilde{E}(\psi, a) = \widetilde{E}(\overline{\psi}, \overline{a}) = 0.$$

Proof. Again for $a \in \mathbb{R}^m_+$ the operator $\widetilde{E}(\cdot, a)$ is strongly monotone uniformly with respect to a as well as hemicontinuous. From this the existence and uniqueness result follows. The estimate

$$c\|\psi\|^2_{H^1} \le \langle \widetilde{E}(\psi, a) - \widetilde{E}(0, a), \psi\rangle \le \Big|\int_\Omega \Big[e(0) + \sum_{i=1}^m a_i p_i'(0) - f\Big]\psi\,\mathrm{d}x\Big| \le c(1 + \|a\|_{\mathbb{R}^m})\|\psi\|_{L^2}$$

yields the assertion on the H^1–norm of ψ. The assertion on the L^∞–norm of ψ is obtained from Lemma 1, for instance. Then the last assertion is obvious. ∎

4. The energy and dissipation functionals

In this section we investigate basic properties of the free energy functional and of other related functionals. First, we define $F_1, F_2 : Y_+ \to \mathbb{R}$ by

$$F_1(u) = \int_\Omega \Big\{\frac{1}{2}|\nabla\psi|^2 + g(\psi) + \sum_{i=1}^m u_i(P_i(\psi) - Q_i(\psi)\psi)\Big\}\,\mathrm{d}x,\ u \in Y_+ \tag{4}$$

where $\psi \in H^1(\Omega)\cap L^\infty(\Omega)$ is the unique solution to the Poisson equation $E(\psi,u)=0$,

$$F_2(u) = \int_\Omega \sum_{i=1}^m \Big\{u_i\Big[\ln\frac{u_i}{p_i(0)}-1\Big]+p_i(0)\Big\}\,\mathrm{d}x,\ \ u\in Y_+, \tag{5}$$

and set

$$F(u)=F_1(u)+F_2(u),\ \ u\in Y_+.$$

The value $F(u)$ can be interpreted as the free energy of the state u. Because of (3) it holds

$$F(u)\ge c\Big\{\|\psi\|^2_{H^1}+\sum_{i=1}^m\|u_i\ln u_i\|_{L^1}-1\Big\},\ \ u\in Y_+. \tag{6}$$

For $u,\overline{u}\in Y_+$ and corresponding $\psi,\overline{\psi}\in H^1(\Omega)$ with $E(\psi,u)=E(\overline{\psi},\overline{u})=0$ we obtain

$$\begin{aligned} F_1(u)-F_1(\overline{u}) &= \int_\Omega\Big\{\sum_{i=1}^m P_i(\overline{\psi})(u_i-\overline{u}_i)+\frac12|\nabla(\psi-\overline{\psi})|^2 \\ &+ \int_{\overline{\psi}}^{\psi}(s-\overline{\psi})\,e'(s)\,\mathrm{d}s-\sum_{i=1}^m u_i\int_{\overline{\psi}}^{\psi}(s-\overline{\psi})\,Q_i'(s)\,\mathrm{d}s\Big\}\,\mathrm{d}x \\ &\ge (P(\overline{\psi}),u-\overline{u})_Y+c\,\|\psi-\overline{\psi}\|^2_{H^1}\ge(P(\overline{\psi}),u-\overline{u})_Y. \end{aligned} \tag{7}$$

From this relation it follows that F_1 is convex and continuous on the convex set Y_+. We extend F_1 to Y by setting $F_1(u)=+\infty$ for $u\in Y\setminus Y_+$. Then the extended functional $F_1:Y\to\overline{\mathbb{R}}$ is proper, convex, lower semicontinuous, and subdifferentiable in each point $u\in Y_+$ where $P(\psi)\in\partial F_1(u)$. Because of properties of its integrand the functional F_2 is convex (see [3]) and continuous (see [7]) on Y_+. Again the extended functional $F_2:Y\to\overline{\mathbb{R}}$, $F_2(u)=+\infty$ for $u\in Y\setminus Y_+$, is proper, convex and lower semicontinuous. For $u,\overline{u}\in Y_+$ with $\overline{u}\ge\delta>0$ we obtain

$$\begin{aligned} F_2(u)-F_2(\overline{u}) &= \int_\Omega\Big\{\sum_{i=1}^m\ln\frac{\overline{u}_i}{p_i(0)}\,(u_i-\overline{u}_i)+\sum_{i=1}^m\int_{\overline{u}_i}^{u_i}\ln\frac{s}{\overline{u}_i}\,\mathrm{d}s\Big\}\,\mathrm{d}x \\ &\ge (\ln\frac{\overline{u}}{p(0)},u-\overline{u})_Y+\|\sqrt{u}-\sqrt{\overline{u}}\|^2_Y\ge(\ln\frac{\overline{u}}{p(0)},u-\overline{u})_Y. \end{aligned} \tag{8}$$

Thus, F_2 is subdifferentiable in points $u\in Y_+$ with $u\ge\delta>0$ and $\ln(u/p(0))\in\partial F_2(u)$. Finally, we have to extend the introduced functionals to the space X^*. We define

$$\widetilde{F}_k=(F_k^*|_X)^*:X^*\to\overline{\mathbb{R}},\ \ k=1,2,$$

where the star denotes the conjugation (see [3])

$$F_k^*(v)=\sup_{u\in Y}\Big\{(u,v)_Y-F_k(u)\Big\},\ \ v\in Y,\quad (F_k^*|_X)^*(u)=\sup_{v\in X}\Big\{\langle u,v\rangle-F_k^*(v)\Big\},\ \ u\in X^*.$$

Easily one verifies that $\widetilde{F}_k$ is proper, convex and lower semicontinuous, that $\widetilde{F}_k(u)=F_k(u)$ for $u\in Y_+$, and that it holds

$$P(\psi)\in\partial\widetilde{F}_1(u),\ \ u\in Y_+,\qquad \ln\frac{u}{p(0)}\in\partial\widetilde{F}_2(u),\ \ u\in X,\ u\ge\delta>0. \tag{9}$$

Omitting the tilde we can summarize the properties of the free energy functional as follows.

Lemma 3. *The functional* $F = F_1 + F_2 : X^* \to \overline{\mathbb{R}}$ *is proper, convex and lower semicontinuous. For* $u \in Y_+$ *it can be evaluated according to* (4), (5)*. The restriction* $F|_{Y_+}$ *is continuous. If* $u \in X$ *and* $u \geq \delta > 0$ *then*

$$\zeta = P(\psi) + \ln \frac{u}{p(0)} = \ln \frac{u}{p(\psi)} \in X, \qquad \zeta \in \partial F(u).$$

Next we study properties of the dual functional $F^* : X \to \overline{\mathbb{R}}$,

$$F^*(\zeta) = \sup_{u \in X^*} \Big\{ \langle u, \zeta \rangle - F(u) \Big\}, \quad \zeta \in X.$$

If F^* is subdifferentiable in ζ, $u \in \partial F^*(\zeta)$, or equivalently, $\zeta \in \partial F(u)$, then (see [3])

$$F^*(\zeta) = \langle u, \zeta \rangle - F(u), \quad \zeta \in \partial F(u). \tag{10}$$

Mainly we are interested in the special situation that $\zeta \in \mathbb{R}^m$. Therefore, let $\zeta \in \mathbb{R}^m$ be given, let $\psi \in H^1(\Omega) \cap L^\infty(\Omega)$ be the solution to the Poisson equation $\widetilde{E}(\psi, \mathrm{e}^\zeta) = 0$, and define $u = p(\psi)\, \mathrm{e}^\zeta$. Obviously, $u \in X$, $u \geq \delta > 0$ and thus $u \in \partial F^*(\zeta)$. By means of (10) we obtain

$$F^*(\zeta) = \int_\Omega \Big\{ \frac{1}{2} |\nabla \psi|^2 + \int_0^\psi e(s)\, \mathrm{d}s - f\psi + \sum_{i=1}^m p_i(0) \Big[\mathrm{e}^{\zeta_i - P_i(\psi)} - 1 \Big] \Big\}\, \mathrm{d}x, \ \zeta \in \mathbb{R}^m.$$

We define the function

$$G = F^*|_{\mathbb{R}^m} : \mathbb{R}^m \to \mathbb{R}.$$

Because of (I), (3) we get the estimate

$$G(\zeta) \geq c \Big\{ \|\psi\|_{H^1}^2 + \|[\zeta - P(\psi)]^+\|_Y^2 - 1 \Big\}, \ \zeta \in \mathbb{R}^m, \tag{11}$$

and for $\zeta, \overline{\zeta} \in \mathbb{R}^m$ with corresponding $\psi, \overline{\psi}$ we find that

$$\begin{aligned} G(\zeta) - G(\overline{\zeta}) &= \int_\Omega \sum_{i=1}^m p_i(\overline{\psi})\, \mathrm{e}^{\overline{\zeta}_i} (\zeta_i - \overline{\zeta}_i)\, \mathrm{d}x + \omega(\zeta, \overline{\zeta}), \\ \omega(\zeta, \overline{\zeta}) &= \int_\Omega \Big\{ \frac{1}{2} |\nabla(\psi - \overline{\psi})|^2 + \int_{\overline{\psi}}^\psi (\psi - s)\, e'(s)\, \mathrm{d}s \\ &\quad - \sum_{i=1}^m p_i(\overline{\psi})\, \mathrm{e}^{\overline{\zeta}_i} \int_{\overline{\psi}}^\psi (\psi - s)\, Q_i'(s)\, \mathrm{d}s \\ &\quad + \sum_{i=1}^m p_i(0) \int_{\overline{\zeta}_i - P_i(\overline{\psi})}^{\zeta_i - P_i(\psi)} (\zeta_i - P_i(\psi) - s)\, \mathrm{e}^s\, \mathrm{d}s \Big\} \mathrm{d}x. \end{aligned}$$

Let $R > 0$ be given. Because of Lemma 2 there exist constants $c_1(R), c_2(R) > 0$ such that for all $\zeta, \overline{\zeta}$ with $\|\zeta\|_{\mathbb{R}^m}, \|\overline{\zeta}\|_{\mathbb{R}^m} \le R$ it holds

$$\begin{aligned} \omega(\zeta,\overline{\zeta}) &\ge c_1(R)\Big\{\|\psi-\overline{\psi}\|^2_{H^1} + \|\zeta-\overline{\zeta}-(P(\psi)-P(\overline{\psi}))\|^2_{L^2}\Big\}, \\ \omega(\zeta,\overline{\zeta}) &\le c_2(R)\,\|\zeta-\overline{\zeta}\|^2_{\mathbb{R}^m}. \end{aligned}$$

From these estimates we derive the following assertions.

Lemma 4. *The function $G = F^*|_{\mathbb{R}^m} : \mathbb{R}^m \to \mathbb{R}$ is strictly convex, continuous and Fréchet differentiable,*

$$\partial G(\zeta) = \int_\Omega \mathrm{e}^\zeta\, p(\psi)\,\mathrm{d}x, \quad \zeta \in \mathbb{R}^m, \quad \widetilde{E}(\psi, \mathrm{e}^\zeta) = 0.$$

A further functional which we are interested in is the dissipation functional, or more precisely, a lower estimate of this functional. We define the set

$$M_D = \Big\{u \in L^\infty_+(\Omega,\mathbb{R}^m) : \sqrt{a} \in X, \text{ where } a = u/p(\psi) \text{ and } E(\psi,u) = 0\Big\}$$

and the functional $D : M_D \to \mathbb{R}$ by

$$\begin{aligned} D(u) &= \int_\Omega \Big\{\sum_{i\in J} 4\,D_i(\psi)p_i(\psi)|\nabla\sqrt{a_i}|^2 \\ &\quad + \sum_{(\alpha,\beta)\in\mathcal{R}} 2\,k_{\alpha\beta}(\psi)|\sqrt{a}^{\,\alpha} - \sqrt{a}^{\,\beta}|^2\Big\}\,\mathrm{d}x, \ u \in M_D. \end{aligned} \tag{12}$$

Lemma 5. *For all $u \in M_D$ it holds $D(u) \ge 0$. If $u \in M_D$ and $D(u) = 0$ then $u = ap(\psi)$ where ψ is the solution to $E(\psi,u) = 0$ and*

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

Proof. The first assertion is obvious. Now let $D(u) = 0$. Since all coefficients in (12) are strictly positive we obtain $a_i = \text{const} \ge 0$, $i \in J$, as well as $a^\alpha = a^\beta$, $(\alpha,\beta) \in \mathcal{R}$. Because of the last assumption in (I) we find that $a_i = \text{const} \ge 0$, $i \in J'$, too. ∎

5. Monotonicity and boundedness of the free energy

According to thermodynamic principles the free energy should monotonously decrease along solutions to the evolution problem (P). This property is indeed obtained from the following theorem.

Theorem 1. *Let (u,ψ) be a solution to* (P) *and set $a = u/p(\psi)$. Then $\sqrt{a} \in L^2_{\mathrm{loc}}(\mathbb{R}_+, X)$, $u(t) \in M_D$* f.a.a. *$t > 0$, and for every $\lambda \in \mathbb{R}_+$ it holds*

$$\mathrm{e}^{\lambda t_2}F(u(t_2)) - \mathrm{e}^{\lambda t_1}F(u(t_1)) - \int_{t_1}^{t_2} \mathrm{e}^{\lambda t}\Big\{\lambda\,F(u(t)) - D(u(t))\Big\}\,\mathrm{d}t \le 0, \quad 0 \le t_1 \le t_2.$$

Proof. 1. Let (u,ψ) be a solution to (P), $\lambda\in\mathbb{R}_+$, $S=[t_1,t_2]$. Then $u\in H^1(S,X^*)$, $\psi\in L^2(S,H^1(\Omega))$, $P(\psi)\in L^2(S,X)$ and $\nabla P(\psi)=Q(\psi)\nabla\psi$. Because of (9) we find $P(\psi(t))\in\partial F_1(u(t))$ f.a.a. $t\in S$. Therefore, the function $t\mapsto F_1(u(t))$ is absolutely continuous on S and there holds the chain rule (see [1])

$$\frac{\mathrm{d}}{\mathrm{d}t}F_1(u(t))=\langle u'(t),P(\psi(t))\rangle \text{ f.a.a. } t\in S.$$

2. We define $u^\delta=u+\delta$ for $\delta>0$. Then $u^\delta\in H^1(S,X^*)$, $\ln(u^\delta/p(0))\in L^2(S,X)$ and $\nabla\ln(u_i^\delta/p_i(0))=\nabla u_i/(u_i+\delta)$, $i\in J$. Because of (9) we find $\ln(u^\delta(t)/p(0))\in\partial F_2(u^\delta(t))$ f.a.a. $t\in S$. Thus, the function $t\mapsto F_2(u^\delta(t))$ is absolutely continuous on S and

$$\frac{\mathrm{d}}{\mathrm{d}t}F_2(u^\delta(t))=\Big\langle u'(t),\ln\frac{u^\delta(t)}{p(0)}\Big\rangle \text{ f.a.a. } t\in S.$$

3. Using these results and setting $\zeta^\delta=\ln(u^\delta/p(\psi))\in L^2(S,X)$ we obtain

$$\mathrm{e}^{\lambda t}\Big[F_1(u(t))+F_2(u^\delta(t))\Big]\Big|_{t_1}^{t_2}=\int_{t_1}^{t_2}\mathrm{e}^{\lambda t}\Big\{\lambda\Big[F_1(u(t))+F_2(u^\delta(t))\Big]+\langle u'(t),\zeta^\delta(t)\rangle\Big\}\,\mathrm{d}t.$$

Here we insert the evolution equation,

$$\langle u'(t),\zeta^\delta(t)\rangle=-\langle A(u(t),\psi(t)),\zeta^\delta(t)\rangle=-\langle A(u^\delta(t),\psi(t)),\zeta^\delta(t)\rangle+h^\delta(t) \text{ f.a.a. } t\in S$$

where $h^\delta=\langle A(u^\delta,\psi)-A(u,\psi),\zeta^\delta\rangle$. We set $a^\delta=u^\delta/p(\psi)=e^{\zeta^\delta}$. Then $\sqrt{a^\delta}\in L^2(S,X)$ and $\nabla\sqrt{a_i^\delta}=\frac{1}{2}\sqrt{a_i^\delta}\,\nabla\zeta_i^\delta$, $i\in J$. Some simple calculation yields

$$D_i(\psi)\left[\nabla u_i^\delta+Q_i(\psi)u_i^\delta\nabla\psi\right]\cdot\nabla\zeta_i^\delta=D_i(\psi)u_i^\delta|\nabla\zeta_i^\delta|^2=4\,D_i(\psi)p_i(\psi)|\nabla\sqrt{a_i^\delta}|^2,\ i\in J,$$

$$R_{\alpha\beta}(u^\delta,\psi)\,(\alpha-\beta)\cdot\zeta^\delta=k_{\alpha\beta}(\psi)\left[\mathrm{e}^{\alpha\cdot\zeta^\delta}-\mathrm{e}^{\beta\cdot\zeta^\delta}\right](\alpha-\beta)\cdot\zeta^\delta\geq 2\,k_{\alpha\beta}(\psi)|\sqrt{a^\delta}^{\,\alpha}-\sqrt{a^\delta}^{\,\beta}|^2,$$

and thus we obtain

$$\int_{t_1}^{t_2}\int_\Omega\mathrm{e}^{\lambda t}\Big\{\sum_{i\in J}4\,D_i(\psi)p_i(\psi)|\nabla\sqrt{a_i^\delta}|^2+\sum_{(\alpha,\beta)\in\mathcal{R}}2\,k_{\alpha\beta}(\psi)|\sqrt{a^\delta}^{\,\alpha}-\sqrt{a^\delta}^{\,\beta}|^2\Big\}\,\mathrm{d}x\mathrm{d}t$$

$$\leq\int_{t_1}^{t_2}\mathrm{e}^{\lambda t}\,\langle A(u^\delta(t),\psi(t)),\zeta^\delta(t)\rangle\,\mathrm{d}t=H^\delta \tag{13}$$

where

$$H^\delta=\int_{t_1}^{t_2}\mathrm{e}^{\lambda t}\Big\{\lambda\Big[F_1(u(t))+F_2(u^\delta(t))\Big]+h^\delta(t)\Big\}\,\mathrm{d}t-\mathrm{e}^{\lambda t}\Big[F_1(u(t))+F_2(u^\delta(t))\Big]\Big|_{t_1}^{t_2}.$$

4. Now let $\delta\to 0$. First, we easily find that

$$H^\delta\to H=\int_{t_1}^{t_2}\mathrm{e}^{\lambda t}\lambda\,F(u(t))\,\mathrm{d}t-\mathrm{e}^{\lambda t}\,F(u(t))\Big|_{t_1}^{t_2}.$$

By Lebesgue's dominated convergence theorem we obtain that $\sqrt{a^\delta} \to \sqrt{a}$ in $L^2(S,Y)$, and at least for a subsequence, $\sqrt{a^\delta} \to \sqrt{a}$ a.e. on $S\times\Omega$. Fatou's lemma yields

$$\begin{aligned}&\int_{t_1}^{t_2}\int_\Omega \mathrm{e}^{\lambda t}\sum_{(\alpha,\beta)\in\mathcal{R}} 2\,k_{\alpha\beta}(\psi)|\sqrt{a}^{\alpha}-\sqrt{a}^{\beta}|^2\mathrm{d}x\mathrm{d}t\\ &\le \liminf_{\delta\to 0}\int_{t_1}^{t_2}\int_\Omega \mathrm{e}^{\lambda t}\sum_{(\alpha,\beta)\in\mathcal{R}} 2\,k_{\alpha\beta}(\psi)|\sqrt{a^\delta}^{\alpha}-\sqrt{a^\delta}^{\beta}|^2\mathrm{d}x\mathrm{d}t. \qquad (14)\end{aligned}$$

Finally, let $i\in J$. Since $\psi\in L^\infty(S,L^\infty)$ and since the sequence H^δ is bounded because of (13) there exists a constant $c>0$ such that $\|\nabla\sqrt{a_i^\delta}\|_{L^2(S,L^2)}\le c$. From this

$$\nabla\sqrt{a_i}\in L^2(S,L^2),\quad \nabla\sqrt{a_i^\delta}\rightharpoonup\nabla\sqrt{a_i}\text{ in }L^2(S,L^2),\quad i\in J,$$

follows (see [13, Proposition 2.4]), and because of the weak lower semicontinuity of continuous quadratic functionals we arrive at

$$\begin{aligned}&\int_{t_1}^{t_2}\int_\Omega e^{\lambda t}\sum_{i\in J}4\,D_i(\psi)p_i(\psi)|\nabla\sqrt{a_i}|^2\,\mathrm{d}x\mathrm{d}t\\ &\le \liminf_{\delta\to 0}\int_{t_1}^{t_2}\int_\Omega e^{\lambda t}\sum_{i\in J}4\,D_i(\psi)p_i(\psi)|\nabla\sqrt{a_i^\delta}|^2\,\mathrm{d}x\mathrm{d}t. \qquad (15)\end{aligned}$$

Hence $\sqrt{a}\in L^2(S,X)$, and from (13) – (15) we obtain $\int_{t_1}^{t_2} e^{\lambda t}D(u(t))\,\mathrm{d}t\le H$. ∎

Corollary 1. *Along any solution* (u,ψ) *to* (P) *the free energy* $F(u)$ *remains bounded from above by its initial value* $F(U)$ *and decreases monotonously,*

$$F(u(t_2))\le F(u(t_1))\le F(U),\quad 0\le t_1\le t_2.$$

Moreover, there exists a constant c depending only on the data such that

$$\begin{aligned}&\sum_{i=1}^m\|u_i\ln u_i\|_{L^\infty(\mathbb{R}_+,L^1(\Omega))}\le c,\quad \|u\|_{L^\infty(\mathbb{R}_+,L^1(\Omega,\mathbb{R}^m))}\le c,\\ &\|\psi\|_{L^\infty(\mathbb{R}_+,H^1(\Omega))}\le c,\quad \|\psi\|_{L^\infty(\mathbb{R}_+,L^\infty(\Omega))}\le c\end{aligned}$$

for any solution to (P).

Proof. The first assertion follows from Theorem 1 by setting $\lambda=0$. The remaining estimates are a consequence of (6) and Lemma 1. ∎

6. Invariants and steady states

We introduce the stoichiometric subspace $\mathcal{S}$ belonging to all reactions,

$$\mathcal{S}=\operatorname{span}\{\alpha-\beta:\ (\alpha,\beta)\in\mathcal{R}\}\subset\mathbb{R}^m.$$

By integrating the continuity equations over $(0,t)\times\Omega$ one easily verifies the following invariance property.

Lemma 6. *If* (u,ψ) *is a solution to* (P) *then* $\int_\Omega \Big\{u(t)-U\Big\}\,\mathrm{d}x \in \mathcal{S}$ *for all* $t\in \mathbb{R}_+$.

Now we ask for steady states belonging to the evolution problem (P) which satisfy such an invariance property, too. Thus we have to solve the following problem.

$$\begin{gathered}A(u,\psi)=0, \quad E(\psi,u)=0, \quad u\geq 0,\\ \int_\Omega \Big\{u-U\Big\}\,\mathrm{d}x\in\mathcal{S},\\ u\in X\cap L^\infty(\Omega,\mathbb{R}^m), \quad \psi\in H^1(\Omega)\cap L^\infty(\Omega).\end{gathered} \tag{S}$$

Lemma 7. *If* (u,ψ) *is a solution to* (S) *then* $u\in M_D$ *and* $D(u)=0$.

Proof. The proof is similar to that of Theorem 1. Let (u,ψ) be a solution to (S), define $a=u/p(\psi)$ and set $u^\delta=u+\delta$, $a^\delta=u^\delta/p(\psi)$, $\zeta^\delta=\ln a^\delta$ where $\delta>0$. Then

$$\zeta^\delta,\ \sqrt{a^\delta}\in X,\ \langle A(u^\delta,\psi),\zeta^\delta\rangle = h^\delta$$

where $h^\delta=\langle A(u^\delta,\psi)-A(u,\psi),\zeta^\delta\rangle\to 0$ if $\delta\to 0$. Furthermore, $\sqrt{a^\delta}\to\sqrt{a}$ in Y and because of the estimate

$$\int_\Omega \Big\{\sum_{i\in J} 4\,D_i(\psi)p_i(\psi)|\nabla\sqrt{a_i^\delta}|^2+\sum_{(\alpha,\beta)\in\mathcal{R}} 2\,k_{\alpha\beta}(\psi)|\sqrt{a^\delta}^{\,\alpha}-\sqrt{a^\delta}^{\,\beta}|^2\Big\}\,\mathrm{d}x\leq\langle A(u^\delta,\psi),\zeta^\delta\rangle$$

we find that $\nabla\sqrt{a_i^\delta}\rightharpoonup\nabla\sqrt{a_i}$ in L^2, $i\in J$. Thus $\sqrt{a}\in X$, $u\in M_D$ and

$$0\leq D(u)\leq\liminf_{\delta\to 0}\langle A(u^\delta,\psi),\zeta^\delta\rangle = 0. \quad\blacksquare$$

Next, we show that there is a correspondence between the set of steady states, i. e. the set of solutions to (S), and the set $\mathcal{A}\subset\mathbb{R}^m$ defined by

$$\begin{aligned}\mathcal{A} \;=\; \Big\{&a\in\mathbb{R}^m_+ :\ a^\alpha=a^\beta\ \forall(\alpha,\beta)\in\mathcal{R},\ \int_\Omega\Big\{u-U\Big\}\,\mathrm{d}x\in\mathcal{S},\\ &\text{where } u=ap(\psi) \text{ and } \psi \text{ is the solution to } \widetilde{E}(\psi,a)=0\Big\}.\end{aligned}$$

Lemma 8. *If* (u,ψ) *is a solution to* (S) *then* $a=u/p(\psi)\in\mathcal{A}$. *Vice versa, if* $a\in\mathcal{A}$ *and* u,ψ *are chosen as in the definition of* $\mathcal{A}$ *then* (u,ψ) *is a solution to* (S).

Proof. The first assertion follows from Lemma 7 and Lemma 5. If $a\in\mathcal{A}$ then obviously $\psi\in H^1(\Omega)\cap L^\infty(\Omega)$, $u=ap(\psi)\in X\cap L^\infty(\Omega,\mathbb{R}^m)$, $u\geq 0$, $\nabla u_i=a_ip_i'(\psi)\nabla\psi=-u_iQ_i(\psi)\nabla\psi$, $i\in J$, $A(u,\psi)=0$, and $E(\psi,u)=\widetilde{E}(\psi,a)=0$. $\blacksquare$

Finally, we show that the set $\mathcal{A} \cap \operatorname{int} \mathbb{R}^m_+$ corresponds to the set of minimizers of the function $G_0 : \mathbb{R}^m \to \overline{\mathbb{R}}$ defined by

$$G_0(\zeta) = G(\zeta) + I_{\mathcal{S}^\perp}(\zeta) - \int_\Omega U \cdot \zeta \,\mathrm{d}x, \quad \zeta \in \mathbb{R}^m.$$

This function is proper, convex and lower semicontinuous, $\operatorname{dom} G_0 = \mathcal{S}^\perp$. Because of the continuity of G (see Lemma 4) we obtain by the Moreau-Rockafellar theorem (see [3]) that

$$\partial G_0(\zeta) = \partial G(\zeta) + \partial I_{\mathcal{S}^\perp}(\zeta) - \int_\Omega U \,\mathrm{d}x,\ \zeta \in \mathbb{R}^m. \tag{16}$$

Lemma 9. *If $a \in \mathcal{A} \cap \operatorname{int} \mathbb{R}^m_+$ then $\zeta = \ln a$ is a minimizer of G_0. Vice versa, if $\zeta \in \mathbb{R}^m$ is a minimizer of G_0 then $a = \mathrm{e}^\zeta \in \mathcal{A} \cap \operatorname{int} \mathbb{R}^m_+$.*

Proof. Because of (16) and Lemma 4, ζ is a minimizer of G_0 if and only if

$$\zeta \in \mathcal{S}^\perp, \quad \partial G(\zeta) - \int_\Omega U \,\mathrm{d}x = \int_\Omega \left\{ \mathrm{e}^\zeta p(\psi) - U \right\} \mathrm{d}x \in \mathcal{S}$$

where ψ is the solution to $\widetilde{E}(\psi, \mathrm{e}^\zeta) = 0$. The relation $\zeta \in \mathcal{S}^\perp$ is equivalent to $(\alpha - \beta) \cdot \zeta = 0\ \forall (\alpha, \beta) \in \mathcal{R}$, or to $(\mathrm{e}^\zeta)^\alpha = (\mathrm{e}^\zeta)^\beta\ \forall (\alpha, \beta) \in \mathcal{R}$. Since the map $\zeta \mapsto \mathrm{e}^\zeta$ is a bijection from $\mathbb{R}^m$ onto $\operatorname{int} \mathbb{R}^m_+$ all assertions of the lemma are obtained. ■

Lemma 10. *The set $\mathcal{A} \cap \operatorname{int} \mathbb{R}^m_+$ contains at most one element. Furthermore, $\mathcal{A} \cap \operatorname{int} \mathbb{R}^m_+ \neq \emptyset$ if and only if the following condition is fulfilled:*

$$\int_\Omega U \cdot \overline{\zeta} \,\mathrm{d}x > 0 \quad \forall \overline{\zeta} \in \mathcal{S}^\perp,\ \overline{\zeta} \geq 0,\ \overline{\zeta} \neq 0. \tag{II}$$

Proof. 1. The first assertion follows from Lemma 9 since the functions G and $G_0|_{\mathcal{S}^\perp}$ are strictly convex.
2. If $a \in \mathcal{A} \cap \operatorname{int} \mathbb{R}^m_+$ then for any $\overline{\zeta} \in \mathcal{S}^\perp,\ \overline{\zeta} \geq 0,\ \overline{\zeta} \neq 0$ we find

$$\int_\Omega U \cdot \overline{\zeta} \,\mathrm{d}x = \int_\Omega \sum_{i=1}^m a_i p_i(\psi) \overline{\zeta}_i \,\mathrm{d}x > 0.$$

3. Now let (II) be fulfilled. According to Lemma 9 we have to show, that there is a minimizer of G_0. It is sufficient to verify the property $G_0(\zeta) \to +\infty$ if $\|\zeta\|_{\mathbb{R}^m} \to +\infty$. Suppose this to be false. Then there exist $R \in \mathbb{R}_+$ and a sequence $\zeta_n \in \mathcal{S}^\perp$ such that

$$\|\zeta_n\|_{\mathbb{R}^m} \to \infty, \quad G_0(\zeta_n) = G(\zeta_n) - \int_\Omega U \cdot \zeta_n \,\mathrm{d}x \leq R.$$

Using (11) this implies

$$c_1 \left\{ \|\psi_n\|^2_{H^1} + \|[\zeta_n - P(\psi_n)]^+\|^2_Y \right\} - (U, \zeta_n)_Y \leq R + c_2. \tag{17}$$

We set $\widetilde{\psi}_n = \psi_n/\|\zeta_n\|$, $\widetilde{\zeta}_n = \zeta_n/\|\zeta_n\|$, and assume that $\widetilde{\zeta}_n \to -\overline{\zeta}$ in $\mathbb{R}^m$ where $\overline{\zeta} \in \mathcal{S}^\perp$, $\overline{\zeta} \neq 0$. Because of (17) we find $\widetilde{\psi}_n \to 0$ in $H^1(\Omega)$, and $\overline{\zeta} \geq 0$ since P is Lipschitz continuous. Again using (17) we obtain $(U, \overline{\zeta})_Y \leq 0$ in contradiction to (II). ∎

There are examples of reaction–diffusion systems with steady states where the corresponding $a \in \mathcal{A}$ belongs to $\partial\mathbb{R}^m_+$ even if condition (II) is satisfied. But in many applications e. g. in semiconductor technology this can not happen. Therefore in our following considerations we shall assume that

$$\mathcal{A} \cap \partial\mathbb{R}^m_+ = \emptyset. \tag{III}$$

Then we may summarize our results concerned with the steady states to (P) as follows.

Theorem 2. *Let the additional assumption* (II) *be fulfilled. Then there exists a solution* (u^*, ψ^*) *to* (S) *with following properties:*

$$a^* = u^*/p(\psi^*) \in \mathbb{R}^m,\ a^* > 0,\ \zeta^* = \ln a^* \in \mathcal{S}^\perp,\ u^* \geq c > 0 \text{ a.e. on } \Omega.$$

If (III) *is fulfilled, too, then there is no other solution to* (S).

Corollary 2. *Assume* (II) *and let* (u^*, ψ^*) *be the solution to* (S) *as in Theorem* 2. *Then for any solution* (u, ψ) *to* (P) *it holds*

$$F(u^*) \leq F(u(t)) \quad \forall t \in \mathbb{R}_+, \quad \int_0^\infty D(u(t))\,\mathrm{d}t \leq F(U) - F(u^*).$$

Proof. This follows from (7), (8) with $\overline{u} = u^*$, $\overline{\psi} = \psi^*$ and from Theorem 1. ∎

7. Exponential decay of the free energy

In this section we shall prove that for any solution to the evolution problem (P) (with the initial value U) the free energy $F(u)$ decays exponentially to its equilibrium value $F(u^*)$ (where u^* belongs to that compatibility class which is generated by U) if the additional assumptions (II) and (III) are fulfilled. This will be a consequence of the following estimate of the free energy by the dissipation functional.

Theorem 3. *Let* (II) *and* (III) *be satisfied. Then for every* $R > 0$ *there exists a constant* $c_R > 0$ *such that*

$$F(u) - F(u^*) \leq c_R\, D(u) \quad \forall u \in M_R$$

where

$$M_R = \Big\{u \in M_D\colon\ F(u) - F(u^*) \leq R,\ \int_\Omega (u - U)\mathrm{d}x \in \mathcal{S}\Big\}.$$

Proof. 1. For $u \in M_R$ let ψ, a be defined by $E(\psi,u)=0$, $a=u/p(\psi)$. First let us note that there is a $c(R)>0$ such that $\|\psi\|_{H^1}, \|\psi\|_{L^\infty} \le c(R)\,\forall u \in M_R$. Setting $\widetilde{F}(u)=F(u)-F(u^*)$ and using (7), (8) and Theorem 2, we obtain the estimates

$$c_1(R)\Big\{\|\sqrt{a/a^*}-1\|_Y^2+\|\psi-\psi^*\|_{H^1}^2\Big\} \le \widetilde{F}(u), \tag{18}$$

$$\widetilde{F}(u) \le c_2(R)\,\|u-u^*\|_Y^2, \tag{19}$$

$$D(u) \ge c_3(R)\widetilde{D}(u),\ \widetilde{D}(u)=\int_\Omega \Big\{\sum_{i\in J}\Big|\nabla\sqrt{a_i/a_i^*}\Big|^2+\sum_{(\alpha,\beta)\in\mathcal{R}}\Big|\sqrt{a/a^*}^{\,\alpha}-\sqrt{a/a^*}^{\,\beta}\Big|^2\Big\}\,\mathrm{d}x$$

for all $u \in M_R$ with positive constants $c_k(R)$. It remains to show that for every $R>0$ there exists a $\widetilde{c}_R>0$ such that

$$\widetilde{F}(u) < \widetilde{c}_R\,\widetilde{D}(u) \quad \forall u \in M_R \setminus \{u^*\}.$$

2. Suppose this assertion to be false. Then there exist $R>0$ and sequences $c_n \in \mathbb{R}$, $u_n \in M_R$ such that $c_n \to +\infty$ and

$$0 < c_n\,\widetilde{D}(u_n) \le \widetilde{F}(u_n) \le R. \tag{20}$$

Let ψ_n, a_n be correspondingly defined. (18), (20) imply that $\|\psi_n\|_{H^1}, \|\sqrt{a_n}\|_Y \le c(R)$, $\widetilde{D}(u_n)\to 0$. Therefore $\psi_n \rightharpoonup \widehat{\psi}$ in H^1, $\psi_n \to \widehat{\psi}$ in L^2. For $i\in J$ we find $\widehat{a}_i \in \mathbb{R}_+$ with $\sqrt{a_{ni}} \to \sqrt{\widehat{a}_i}$ in H^1 and in each L^p. For $i \in J'$ we have at least $a_{ni}\to\widehat{a}_i\in\mathbb{R}_+$ in L^2 since for such i there is a special reaction for which

$$\int_\Omega \Big|\prod_{j\in J}\sqrt{a_{nj}/a_j^*}^{\,\alpha_j}-a_{ni}/a_i^*\Big|^2\,\mathrm{d}x \to 0.$$

Fatou's lemma ensures that $\widehat{a}^\alpha=\widehat{a}^\beta\,\forall(\alpha,\beta)\in\mathcal{R}$. Setting $\widehat{u}=\widehat{a}p(\widehat{\psi})$ we get $u_n\to\widehat{u}$ in Y, and thus $\int_\Omega(\widehat{u}-U)\,\mathrm{d}x\in\mathcal{S}$. The estimate $\|\psi_{n+p}-\psi_n\|_{H^1} \le c\,\|u_{n+p}-u_n\|_Y$ shows that $\psi_n \to \widehat{\psi}$ in H^1. Using properties of E we conclude that $E(\psi_n,\widehat{u}) \rightharpoonup E(\widehat{\psi},\widehat{u})$ in $(H^1)^*$, $E(\psi_n,\widehat{u})\to 0$ in $(H^1)^*$. Thus $E(\widehat{\psi},\widehat{u})=\widetilde{E}(\widehat{\psi},\widehat{a})=0$ is obtained. Summarizing, we have found that $\widehat{a}\in\mathcal{A}$. Now assumption (III) ensures that $\widehat{a}=a^*$, and correspondingly $\widehat{u}=u^*$, $\widehat{\psi}=\psi^*$. From (19) we conclude that $\widetilde{F}(u_n)\to 0$.

3. We set

$$w_n=\sqrt{a_n/a^*}-1,\ \lambda_n=\sqrt{\widetilde{F}(u_n)},\ b_n=w_n/\lambda_n,\ y_n=(u_n-u^*)/\lambda_n,\ z_n=(\psi_n-\psi^*)/\lambda_n.$$

In the formula for the lower bound of the dissipation rate

$$\widetilde{D}(u_n)=\int_\Omega\Big\{\sum_{i\in J}|\nabla w_{ni}|^2+\sum_{(\alpha,\beta)\in\mathcal{R}}|(1+w_n)^\alpha-(1+w_n)^\beta|^2\Big\}\,\mathrm{d}x$$

we use the binomial expansion

$$\prod_{i\in I}(1+w_{ni})^{\alpha_i}=1+\sum_{i\in I}\alpha_i w_{ni}+\omega(w_n), \quad \frac{1}{\lambda_n}\,|\omega(w_n)| \le c\sum_{i\in I}\Big\{\lambda_n|b_{ni}|^2+\lambda_n^{p_\alpha-1}|b_{ni}|^{p_\alpha}\Big\}$$

where $p_\alpha = \max\{2, \sum_{i\in I}\alpha_i\}$. (18), (20) imply that $\|z_n\|_{H^1}, \|b_n\|_Y \le c(R)$, $\widetilde{D}(u_n)/\lambda_n^2 \to 0$. Therefore $z_n \rightharpoonup \widehat{z}$ in H^1, $z_n \to \widehat{z}$ in L^2. Now, for $i \in J$ we find $\widehat{b}_{ni} \in \mathbb{R}_+$ with $b_{ni} \to \widehat{b}_i$ in H^1 and in each L^p, moreover $\lambda_n \|b_{ni}^2\|_{L^2} \to 0$. For $i \in J'$ from

$$\int_\Omega \Big| \frac{1}{\lambda_n}\Big\{ \prod_{j\in J}(1+w_{nj})^{\alpha_j} - 1\Big\} - 2b_{ni} - \lambda_n b_{ni}^2 \Big|^2 \,\mathrm{d}x \to 0$$

it follows that $2b_{ni} + \lambda_n b_{ni}^2 \to 2\widehat{b}_i \in \mathbb{R}_+$ in L^2, and because of the estimate

$$\|b_{ni} - \widehat{b}_i\|_{L^2} \le c(R)\,(\|2b_{ni} + \lambda_n b_{ni}^2 - 2\widehat{b}_i\|_{L^2} + \lambda_n \|b_{ni}\|_{L^2})$$

we get $b_{ni} \to \widehat{b}_i$ in L^2 as well as $\lambda_n \|b_{ni}^2\|_{L^2} \to 0$. Fatou's lemma yields $(\alpha - \beta)\cdot \widehat{b} = 0\ \forall (\alpha,\beta) \in \mathcal{R}$, or in other words, $\widehat{b} \in \mathcal{S}^\perp$. Setting $\widehat{y} = a^* p(\psi^*)(2\widehat{b} - Q(\psi^*)\widehat{z})$ we get

$$\|y_n - \widehat{y}\|_Y \le c(R)\Big\{ \|b_n - \widehat{b}\|_Y + \|z_n - \widehat{z}\|_{L^2} + \lambda_n \Big(\sum_{i=1}^m \|b_{ni}^2\|_{L^2} + 1\Big)\Big\},$$

and thus $y_n \to \widehat{y}$ in Y. Consequently, $\int_\Omega \widehat{y}\,\mathrm{d}x \in \mathcal{S}$ and $(\widehat{b}, \widehat{y})_Y = 0$. Finally, we obtain

$$0 \ge \frac{1}{\lambda_n^2}\langle E(\psi^*, u_n) - E(\psi_n, u_n), \psi_n - \psi^*\rangle = -\int_\Omega \sum_{i=1}^m Q_i(\psi^*) z_n y_{ni}\,\mathrm{d}x,$$

and using $(\widehat{b}, \widehat{y})_Y = 0$, in the limit we arrive at

$$0 \ge -\int_\Omega \sum_{i=1}^m Q_i(\psi^*)\widehat{z}\widehat{y}_i\,\mathrm{d}x = \int_\Omega \sum_{i=1}^m (2\widehat{b}_i - Q_i(\psi^*)\widehat{z})\,\widehat{y}_i\,\mathrm{d}x = \int_\Omega \sum_{i=1}^m \frac{1}{a_i^* p_i(\psi^*)}\,|\widehat{y}_i|^2\,\mathrm{d}x.$$

Therefore $\widehat{y} = 0$, and (19) gives the contradiction $1 \le c_2(R)\|y_n\|_Y^2 \to 0$. ■

Corollary 3. *Let the assumptions* (II), (III) *be fulfilled. Then along any solution* (u, ψ) *to* (P) *the free energy* $F(u)$ *decays exponentially to its equilibrium value* $F(u^*)$,

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

where λ *depends only on the data. Moreover, there is a constant* c *such that*

$$\|u(t) - u^*\|_{L^1(\Omega,\mathbb{R}^m)},\ \|\psi(t) - \psi^*\|_{H^1(\Omega)} \le c\,\mathrm{e}^{-\lambda t/2} \quad \forall t \ge 0$$

for any solution to (P).

Proof. Because of Corollary 1 and Lemma 6 for $R = \max\{1, F(U) - F(u^*)\} > 0$ it holds $u(t) \in M_R$ f.a.a. $t > 0$. We set $\lambda = 1/c_R$ and with Theorem 3, Theorem 1 the first assertion is obtained. In Theorem 2 have we stated that $\zeta^* \in \mathcal{S}^\perp$. Then the estimates follow from (7), (8) by setting there $\overline{u} = u^*$, $\overline{\psi} = \psi^*$. ■

8. Remarks

Remark 1. We consider a special version of the pair diffusion models in [2,4]. The meaning of the species and the used reactions are outlined in Fig. 1. Here $m = 5$, $i = 1, \dots, 5$, or in the notation of Fig. 1, $i = A, I, V, AI, AV$, $J = \{2,3,4,5\}$, $J' = \{1\}$. The functions p_i, Q_i are given by (2), D_i, $k_{\alpha\beta}$ are similar averaged quantities and $e(\psi) = c \sinh \psi$. These functions have all properties which are required in (I). Next we find that $\dim \mathcal{S} = 3$, $\dim \mathcal{S}^\perp = 2$, $\mathcal{S}^\perp = \operatorname{span}\{(1,0,0,1,1),(0,1,-1,1,-1)\}$ such that there are two invariants the value of which is fixed by the initial state, namely

$$I_1(t) = \int_\Omega [u_A(t) + u_{AI}(t) + u_{AV}(t)]\,\mathrm{d}x = I_1(0),$$

$$I_2(t) = \int_\Omega [u_I(t) - u_V(t) + u_{AI}(t) - u_{AV}(t)]\,\mathrm{d}x = I_2(0) \quad \forall t \in \mathbb{R}_+.$$

Condition (II) means that $I_1(0) > 0$, and we easily verify that then assumption (III) is fulfilled, too. Thus our results can be applied to this special model.

Remark 2. In (1) the boundary conditions for the first set of continuity equations can be replaced by the following ones:

$$\nu \cdot j_i = \sum_{(\alpha,\beta)\in\mathcal{R}^\Gamma} (\alpha_i - \beta_i)\, R^\Gamma_{\alpha\beta} \quad \text{on } (0,\infty)\times\partial\Omega,\ i \in J,$$

$$R^\Gamma_{\alpha\beta}(x,u,\psi) = k^\Gamma_{\alpha\beta}(x,\psi)\,\Big[\prod_{i=1}^m a_i^{\alpha_i} - \prod_{i=1}^m a_i^{\beta_i}\Big],\ x \in \partial\Omega,\ u \in \mathbb{R}^m,\ \psi \in \mathbb{R},\ a_i = \frac{u_i}{p_i(\psi)},$$

where $(\alpha,\beta) \in \mathcal{R}^\Gamma$ and $\mathcal{R}^\Gamma \subset \{(\alpha,\beta) \in \mathbb{Z}_+^m \times \mathbb{Z}_+^m : \alpha_i = \beta_i = 0\, \forall i \in J'\}$ describes a set of additional boundary reactions. We assume that for each $(\alpha,\beta) \in \mathcal{R}^\Gamma$ the function $k^\Gamma_{\alpha\beta} : \partial\Omega \times \mathbb{R} \to \mathbb{R}$ satisfies the Carathéodory conditions and

$$c_{1,R}(x) \le k^\Gamma_{\alpha\beta}(x,\psi) \le c_{2,R}(x) \text{ f.a.a. } x \in \partial\Omega,\ \forall \psi \in \mathbb{R},\ |\psi| \le R,$$

$$c_{1,R},\ c_{2,R} \in L^\infty_+(\partial\Omega),\ \|c_{1,R}\|_{L^1(\partial\Omega)} > 0.$$

All boundary reactions must be included into the definition of the sets $\mathcal{S}$, $\mathcal{A}$, and in the definition of A, D boundary integrals have to be added. Then all assertions of the paper, especially the assertions of Corollary 1 – Corollary 3 remain valid.

Remark 3. Testing the Poisson equation $E(\psi,u) = 0$ by $\overline{\psi} = 1$ the global electroneutrality condition

$$\int_\Omega \Big[e(\psi(t)) - \sum_{i=1}^m Q_i(\psi(t))\, u_i(t) - f\Big]\,\mathrm{d}x = 0\ \forall t \in \mathbb{R}_+ \tag{21}$$

is obtained. If we want to use other boundary conditions for the Poisson equation in (1) then condition (21) must be taken onto account, too. Therefore, as in [7] we consider mixed boundary conditions of the form

$$\psi = \zeta_0 \quad \text{on } (0,\infty)\times\Gamma_D, \quad \nu\cdot\nabla\psi + \tau\psi = \tau\zeta_0 \quad \text{on } (0,\infty)\times\Gamma_N$$

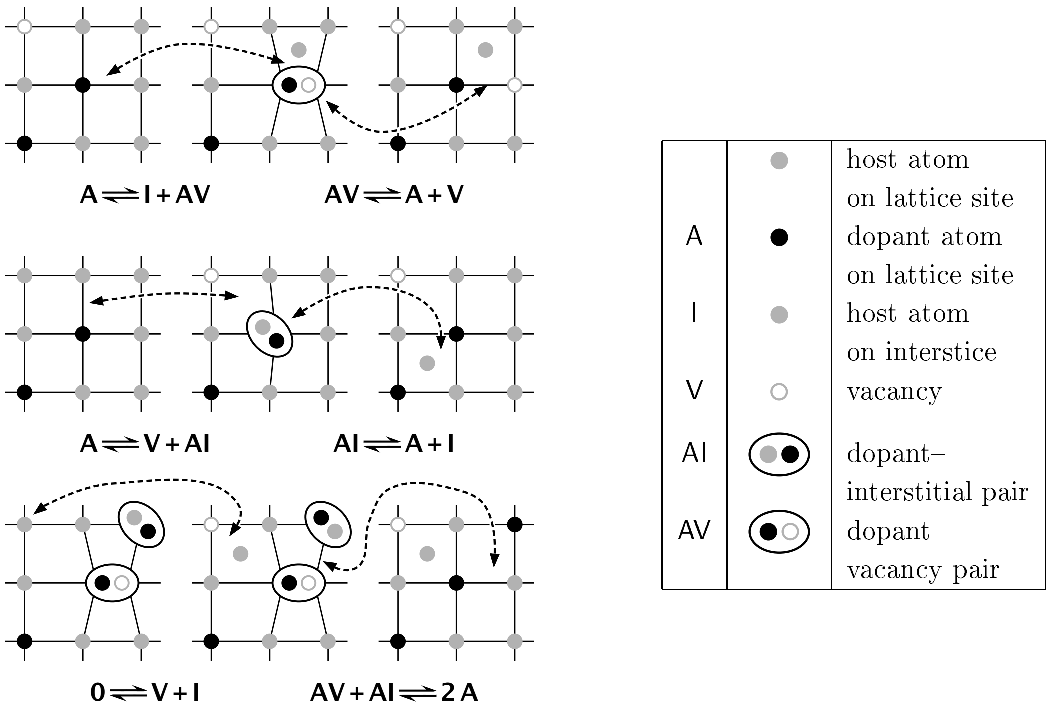

Fig. 1: Species and reactions in the pair diffusion model (see [2,4]). The corresponding reaction rates are given by

$$
\begin{aligned}
R_{\alpha\beta} &= k_{\alpha\beta}(\psi)\,(a_A - a_I\,a_{AV}), & R_{\alpha\beta} &= k_{\alpha\beta}(\psi)\,(a_{AV} - a_A\,a_V),\\
R_{\alpha\beta} &= k_{\alpha\beta}(\psi)\,(a_A - a_V\,a_{AI}), & R_{\alpha\beta} &= k_{\alpha\beta}(\psi)\,(a_{AI} - a_A\,a_I),\\
R_{\alpha\beta} &= k_{\alpha\beta}(\psi)\,(1 - a_V\,a_I), & R_{\alpha\beta} &= k_{\alpha\beta}(\psi)\,(a_{AV}\,a_{AI} - a_A^2)
\end{aligned}
$$

where e. g. for the first reaction $\alpha = (1,0,0,0,0)$, $\beta = (0,1,0,0,1)$ and for the last one $\alpha = (0,0,0,1,1)$, $\beta = (2,0,0,0,0)$.

where the new unknown quantity $\zeta_0 : \mathbb{R}_+ \to \mathbb{R}$ (the electrochemical potential of electrons, i. e. the Fermi level) has to be determined by means of the nonlocal constraint (21). We assume that

$$
\begin{aligned}
&\Gamma_D,\, \Gamma_N \text{ are disjoint open subsets of } \partial\Omega,\ \partial\Omega = \overline{\Gamma_D} \cup \overline{\Gamma_N},\\
&\overline{\Gamma_D} \cap \overline{\Gamma_N} \text{ consists of finitely many points},\\
&\tau \in L^\infty_+(\Gamma_N),\ \operatorname{mes}\Gamma_D + \|\tau\|_{L^1(\Gamma_N)} > 0.
\end{aligned}
$$

The definition of E must be changed (see [7]) and F, F^* contain an additional boundary integral. Again, all assertions of Corollary 1 – Corollary 3 remain valid.

Remark 4. As in [6] analogous energy estimates and asymptotic properties can be derived for a discrete–time version of (1) using an implicit scheme of first order.

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