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Uniform exponential decay for reaction-diffusion systems with complex-balanced mass-action kinetics

Dedicated to Bernold Fiedler on the occasion of his sixtieth birthday

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Abstract

We consider reaction-diffusion systems on a bounded domain with no-flux boundary conditions. All reactions are given by the mass-action law and are assumed to satisfy the complex-balance condition. In the case of a diagonal diffusion matrix, the relative entropy is a Liapunov functional. We give an elementary proof for the Liapunov property as well a few explicit examples for the condition of complex or detailed balancing.

We discuss three methods to obtain energy-dissipation estimates, which guarantee exponential decay of the relative entropy, all of which rely on the log-Sobolev estimate and suitable handling of the reaction terms as well as the mass-conservation relations. The three methods are (i) a convexification argument based on the author's joint work with Haskovec and Markowich, (ii) a series of analytical estimates derived by Desvillettes, Fellner, and Tang, and (iii) a compactness argument of developed by Glitzky and Hünlich.

1 Introduction

We consider reaction-diffusion system (RDS) for concentrations $\boldsymbol{c} = (c_1, \dots, c_I) \in [0,\infty[^I$ of species $\mathcal{A}_1, \dots, \mathcal{A}_I$ that diffuse in a bounded Lipschitz domain $\Omega \subset \mathbb{R}^d$ (with normalized volume $|\Omega| = 1$) and may react according to the mass-action law. Together with the no-flux boundary condition the system under consideration reads

$$\dot{\boldsymbol{c}} = \operatorname{diag}(\delta_1, ..., \delta_I)\Delta \boldsymbol{c} + \boldsymbol{R}(\boldsymbol{c}) \text{ in } \Omega, \quad \nu \cdot \nabla \boldsymbol{c} = 0 \text{ on } \partial\Omega. \tag{1.1}$$

Here $\delta_i > 0$ are positive diffusion constants, and the reaction term $\boldsymbol{R} : [0,\infty[^I \to \mathbb{R}^I$ will be specified later.

A function $F : [0,\infty[^I \to \mathbb{R}$ is a Liapunov function for the reaction-rate equation (RRE) $\dot{\boldsymbol{c}} = \boldsymbol{R}(\boldsymbol{c})$ (which is a ODE) if $\mathrm{D}F(\boldsymbol{c}) \cdot \boldsymbol{R}(\boldsymbol{c}) \le 0$. It was already observed in [Ali79, Lem. 4.1] that, if additionally the symmetric part of $\mathbb{D}\,\mathrm{D}^2F(\boldsymbol{c})$ is positive semidefinite for all $\boldsymbol{c}$, we obtain the Liapunov function

$$\mathcal{F}(\boldsymbol{c}(\cdot)) := \int_\Omega F(\boldsymbol{c}(x))\,\mathrm{d}x$$

for the RDS (1.1). Indeed, along solutions $\boldsymbol{c}(t)$ we have

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{F}(\boldsymbol{c}(t)) = \int_\Omega \mathrm{D}F(\boldsymbol{c}) \cdot \boldsymbol{R}(\boldsymbol{c})\,\mathrm{d}x - \int_\Omega \nabla \boldsymbol{c} : \big(\mathbb{D}\,\mathrm{D}^2F(\boldsymbol{c})\big)\nabla \boldsymbol{c}\,\mathrm{d}x =: -\mathcal{D}(\boldsymbol{c}),$$

with $\mathbb{D} := \operatorname{diag}(\delta_i)$, where the boundary terms disappear because of the no-flux boundary conditions. Obviously, the first term is non-positive since F is a Liapunov function for the RRE, and the second term is non-positive by the assumption on $\mathbb{D}\,\mathrm{D}^2F(\boldsymbol{c})$.

In [Ali79] there is also a general discussion about well-posedness and positivity of solutions, which we do not address here. For general theory of existence we refer to the survey [Pie10] and the very general, recent construction of renormalized solutions in [Fis15]. The latter work as well as the existence results for an improved Nernst-Planck-Poisson system in [DD*16, Dru16] essentially use variants of the energy-dissipation

estimates investigated here more quantitatively. We also refer to [FGZ14, GeZ10] for existence results based on the logarithmic Sobolev inequality, which are close in spirit to our methods discussed below.

We restrict our attention solely to the question of providing quantitative decay estimates via energy-dissipation estimates of the form

$$\mathcal{D}(\boldsymbol{c}) \geq K\mathcal{F}(\boldsymbol{c}) \tag{1.2}$$

for some $K > 0$. Then, for sufficiently well-behaved solutions we have $\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{F}(\boldsymbol{c}(t)) = -\mathcal{D}(\boldsymbol{c}(t)) \leq -K\mathcal{F}(\boldsymbol{c}(t))$, which implies the exponential estimate $\mathcal{F}(\boldsymbol{c}(t)) \leq \mathrm{e}^{-Kt}\mathcal{F}(\boldsymbol{c}(0))$ for all $\boldsymbol{c}(0)$ and all $t > 0$. We will compare three methods and show that the methods developed originally for RDS satisfying the detailed-balance condition immediately generalize to RDS satisfying the more general complex-balance condition. This condition is consistent with damped oscillatory behavior which is common in many chemical systems and which may even lead to Hopf bifurcations when an originally closed system is controlled by suitable boundary conditions, see [Fie83, Fie85].

First methods for obtaining exponential decay for RDS were developed in [Grö83, Grö86], and a variant for semiconductor models was developed in [GGH94, GGH96, GlH97]. There as well as in the series of papers [DeF06, DeF07, DFT16] (see also the reference therein) and in [MHM15, HH*16, MiM16] the essential structure arises from the restriction to reaction terms in $\boldsymbol{R}(\boldsymbol{c})$ given in terms of the mass action law. More precisely, we consider R reactions in the form

$$\boldsymbol{R}(\boldsymbol{c}) = \sum_{r=1}^{R} \kappa_r \boldsymbol{c}^{\boldsymbol{\alpha}^{S_r}} \left(\boldsymbol{\alpha}^{P_r} - \boldsymbol{\alpha}^{S_r}\right) \text{ with monomials } \boldsymbol{c}^{\boldsymbol{\gamma}} := c_1^{\gamma_1} c_2^{\gamma_2} \cdots c_I^{\gamma_I},$$

where the stoichiometric vectors $\boldsymbol{\alpha}^{S_r}, \boldsymbol{\alpha}^{P_r} \in \mathbb{N}_0^I$ for the rth reaction correspond to the substrate (educt) complex and the product complex, respectively, see Section 2, where we also discuss the conditions of detailed balancing and the weaker notion of complex balancing with respect to a positive equilibrium concentration $\boldsymbol{c}_* = (c_1^*, ..., c_I^*) \in]0, \infty[^I$, see Section 2.2. The surprising result, first established in [HoJ72, Thm. 6A], is that for mass-action RRE satisfying the complex-balance condition, the relative entropy

$$F(\boldsymbol{c}) = H(\boldsymbol{c}|\boldsymbol{c}_*) := \sum_{i=1}^{I} c_i^* \lambda_{\mathrm{B}}(c_i/c_i^*) \text{ with } \lambda_{\mathrm{B}}(z) := z\log z - z + 1$$

is a Liapunov function. Indeed, we give a simple and self-contained proof of this fact in Proposition 2.3. Moreover, F is convex and $\mathbb{D}\,\mathrm{D}^2F(\boldsymbol{c})$ is semidefinite, since $\mathbb{D}$ and $\mathrm{D}^2F(\boldsymbol{c})$ are diagonal, hence we have a positive dissipation functional $\mathcal{D}$ taking the form

$$\mathcal{D}(\boldsymbol{c}) = \mathcal{D}_{\mathrm{D}}(\boldsymbol{c}) + \mathcal{D}_{\mathrm{R}}(\boldsymbol{c}) := \int_\Omega \sum_{i=1}^{I} \delta_i \frac{|\nabla c_i|^2}{c_i}\,\mathrm{d}x + \int_\Omega \boldsymbol{R}(\boldsymbol{c})\cdot\big(\log(c_i/c_i^*)\big)_i\,\mathrm{d}x.$$

In general an energy-dissipation estimate like (1.2) is not to be expected, since there are additional conservation laws. Defining the stoichiometric subspace $\mathbb{S} := \mathrm{span}\{\,\boldsymbol{\alpha}^{S_r} - \boldsymbol{\alpha}^{P_r}\,|\,r = 1, .., R\,\} \subset \mathbb{R}^I$ we can choose a matrix Q such that $\mathrm{kernel}(\mathsf{Q}) = \mathbb{S}$ and $\mathrm{range}(\mathsf{Q}^\top) = \mathbb{S}^\perp$.

Then, for the RRE $\dot{\boldsymbol{c}} = \boldsymbol{R}(\boldsymbol{c})$ the value $\mathsf{q} = \mathsf{Q}\boldsymbol{c}(t)$ is constant along solutions, and moreover the no-flux boundary conditions in the RDS (1.1) guarantee that $\mathsf{q} = \mathcal{Q}(\boldsymbol{c}(t)) = \int_\Omega \mathsf{Q}\boldsymbol{c}(t,x)\,\mathrm{d}x$ is constant along solutions.

Thus, the correct adaptation of the energy-dissipation estimate (1.2) reads

$$\begin{aligned} &\forall\,\mathsf{q}\ \exists\, K(\mathsf{q})>0\ \forall\,\boldsymbol{c}\in \mathrm{L}^1_{\geq 0}(\Omega) \text{ with } \mathcal{Q}(\boldsymbol{c})=\mathsf{q}: \quad \mathcal{D}(\boldsymbol{c}) \geq K(\mathsf{q})\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}),\\ &\text{where } \mathcal{H}_{\mathsf{q}}(\boldsymbol{c}) := \int_\Omega H(\boldsymbol{c}(x)|\boldsymbol{w}_{\mathsf{q}})\,\mathrm{d}x. \end{aligned} \tag{1.3}$$

Here $\boldsymbol{w}_{\mathsf{q}}$ is the unique minimizer of $\boldsymbol{c}\mapsto H(\boldsymbol{c}|\boldsymbol{c}_*)$ under the constraint $\mathsf{Q}\boldsymbol{c}=\mathsf{q}$, see Section 3.1 for more details.

Our first result shows that the convexity method introduced in [MHM15] can be generalized from the case with detailed balancing to the case with complex balancing. It is based on the scalar-valued logarithmic Sobolev inequality

$$\int_\Omega \frac{|\nabla u(x)|^2}{u(x)}\,\mathrm{d}x \geq \rho_{\mathrm{lSo}}(\Omega)\int_\Omega H(u(x)|\overline{u})\,\mathrm{d}x, \text{ where } \overline{u}=\int_\Omega u(x)\,\mathrm{d}x$$

(recall $|\Omega|=1$) and the nontrivial assumption that

$$\exists\,\mu_1,\dots,\mu_I\geq 0: \quad \boldsymbol{c}\mapsto \sum_{i=1}^I \mu_i\lambda_{\mathrm{B}}(c_i)+\boldsymbol{R}(\boldsymbol{c})\cdot\big(\log(c_j/c_j^*)\big)_j \text{ is convex.}$$

Then, we obtain a simple lower bound for the decay rate $K(\mathsf{q})$ in (1.3), namely

$$K(\mathsf{q}) \geq \min\Big\{\, k_{\mathrm{R}}(\mathsf{q}), \delta_i\rho_{\mathrm{lSo}}(\Omega)\,\frac{k_{\mathrm{R}}(\mathsf{q})}{\mu_i+k_{\mathrm{R}}(\mathsf{q})} \;\Big|\; i=1,\dots,I\,\Big\},$$

where $k_{\mathrm{R}}(\mathsf{q})$ is the constant k_{R} for $\boldsymbol{R}(\boldsymbol{c})\cdot\big(\log(c_i/c_i^*)\big)_i \geq k_{\mathrm{R}}H(\boldsymbol{c}|\boldsymbol{w}_{\mathsf{q}})$ under the constraint $\mathsf{Q}\boldsymbol{c}=\mathsf{q}$. As observed in [MHM15, Sec. 4.2], the case $\mu_i=0$ is relevant for linear reactions, which is the case for Markov processes; then the decay rate for the RDS is simply given by the minimum of the reactive decay and the diffusive decays of the different species.

In Section 3.3 we consider the nonlinear two-species model

$$\dot{c}_1=\delta_1\Delta c_1+\kappa a\big(c_2^b-c_1^a\big), \quad \dot{c}_2=\delta_2\Delta c_2+\kappa b\big(c_1^a-c_2^b\big) \text{ in } \Omega, \qquad \nu\cdot\nabla c_j=0 \text{ on } \partial\Omega,$$

and show that the convexity method is applicable in the case $b=a\in[1,2]$ (cf. Theorem 3.3) and in the case $a=1$ and $b\in[1,m^*[$ with $m^*\approx 22.06$ by choosing $\mu_2=0$ and $\mu_1=\kappa\widehat{\mu}(b)$ where $\widehat{\mu}(b)\approx(b-1)/(1-b/m^*)$ (cf. Theorem 3.4).

In Section 3.4 we shortly summarize the general method of Desvillettes, Fellner, and Tang which is based on a series of papers which started with [DeF06, DeF07] and first studied complex-balanced RDS in [DFT16].

Finally, Section 4 is devoted to an even more general method that is based on a compactness argument providing a positive constant $\widetilde{K}(\mathsf{q},M)$ such that

$$\begin{aligned} &\forall\,\mathsf{q}\ \forall\,M>0\ \exists\,\widehat{K}(\mathsf{q},M)>0\ \forall\,\boldsymbol{c}\in\mathrm{L}^1_{\geq 0}(\Omega) \text{ with } \mathcal{Q}(\boldsymbol{c})=\mathsf{q}:\\ &\qquad\qquad \mathcal{H}_{\mathsf{q}}(\boldsymbol{c})\leq M \implies \mathcal{D}(\boldsymbol{c})\geq \widetilde{K}(\mathsf{q},M)\,\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}). \end{aligned} \tag{1.4}$$

The method is based on ideas first developed in [GGH94, GGH96] and explained in detail in [GlH97]. Since that work is devoted to the more complicated case of electrically charged particles interacting via the Poisson equation, the theory there is restricted to the two-dimensional case $\Omega \subset \mathbb{R}^2$. Here we show that this restriction is not necessary in the case without charge interactions.

As an outlook, we mention that in this work the three methods are discussed for RDS at constant temperature, however in recent work generalizations to the non-isothermal case were developed, see [HH*16, MiM16]. For this, it is advantageous to use the internal energy $u \in \mathbb{R}$ as an additional variable rather than the more traditional choice of the absolute temperature θ. The main point is to allow that in the so-called energy-reaction-diffusion systems the equilibrium states $\boldsymbol{c}_* = \boldsymbol{w}(u)$ for the reactions depend on the internal energy u in a suitable way, namely $w_i'(u) \geq 0$ and $w_i''(u) \leq 0$.

2 Complex-based description of mass-action kinetics

2.1 Reaction complexes and stoichiometric subspaces

Each reaction is given in terms of stoichiometric coefficients in the form

$$\alpha_1 \mathcal{A}_1 + \cdots + \alpha_I \mathcal{A}_I \ \rightharpoonup \ \widetilde{\alpha}_1 \mathcal{A}_1 + \cdots + \widetilde{\alpha}_I \mathcal{A}_I,$$

where the vector $\boldsymbol{\alpha} = (\alpha_1, ..., \alpha_I)^\top \in \mathbb{N}_0^I$ describes the reactant species (also called educts), defining the substrate complex, and $\widetilde{\boldsymbol{\alpha}} = (\widetilde{\alpha}_1, ..., \widetilde{\alpha}_I)^\top \in \mathbb{N}_0^I$ describes the product species, defining the product complex. By

$$\mathcal{C}^j = \alpha_1^j \mathcal{A}_1 + \alpha_2^j \mathcal{A}_2 + \cdots + \alpha_I^j \mathcal{A}_I \quad \text{with } j = 1, ..., C,$$

we denote the set of all occurring complexes, either as substrate complex or product complex. Thus, all the R reactions have the form

$$\mathcal{C}^j \ \overset{k_{jl}}{\rightharpoonup} \ \mathcal{C}^l \quad \text{or} \quad \mathcal{C}^{S_r} \ \overset{\kappa_r}{\rightharpoonup} \ \mathcal{C}^{P_r}.$$

In the first case we allow $k_{jl} = 0$ if there is no reaction with substrate complex $\mathcal{C}^j$ and product complex $\mathcal{C}^l$. In the second case we impose $\kappa_r > 0$ and denote by $S_r, P_r \in \{1, ..., C\}$ the index of the substrate and product complex, respectively. By definition we have $\kappa_r = k_{S_r P_r}$, and we always assume $k_{jl} = 0$ or $S_r \neq P_r$. Thus, the RRE of the associated mass-action kinetics reads

$$\dot{\boldsymbol{c}} \ = \ \boldsymbol{R}(\boldsymbol{c}) \quad = \quad \sum_{j,l=1}^{C} k_{jl} \boldsymbol{c}^{\boldsymbol{\alpha}^j} \big(\boldsymbol{\alpha}^l - \boldsymbol{\alpha}^j\big) \quad = \quad \sum_{r=1}^{R} \kappa_r \boldsymbol{c}^{\boldsymbol{\alpha}^{S_r}} \big(\boldsymbol{\alpha}^{P_r} - \boldsymbol{\alpha}^{S_r}\big). \tag{2.1}$$

The stoichiometric subspace is defined via

$$\mathbb{S} := \operatorname{span}\Big\{ \boldsymbol{\alpha}^{P_r} - \boldsymbol{\alpha}^{S_r} \ \Big| \ r = 1, ..., R \Big\},$$

which implies that $\boldsymbol{R}(\boldsymbol{c}) \in \mathbb{S}$ for all $\boldsymbol{c}$. Typically we have $\dim \mathbb{S} < I$, which means that $[0, \infty]^I$ decomposes into flow-invariant subset. To describe these sets we choose a matrix $\mathsf{Q} \in \mathbb{R}^{I \times m}$ with $m = I - \dim \mathbb{S}$ such that

$$\operatorname{kernel}(\mathsf{Q}) = \mathbb{S} \quad \text{and} \quad \operatorname{range}\big(\mathsf{Q}^\top\big) = \mathbb{S}^\perp := \{ \boldsymbol{\xi} \in \mathbb{R}^I \mid \boldsymbol{\xi} \cdot \boldsymbol{v} = 0 \text{ for all } \boldsymbol{v} \in \mathbb{S} \}. \tag{2.2}$$

We now define the flow-invariant sets $\boldsymbol{C}_{\mathsf{q}} \subset [0,\infty[^I$, called stoichiometric compatibility class, and the set $\mathfrak{Q}$ of relevant $\mathsf{q} \in \mathbb{R}^m$ via

$$\boldsymbol{C}_{\mathsf{q}} := \{\, \boldsymbol{c} \in [0,\infty[^I \mid \mathsf{Q}\boldsymbol{c} = \mathsf{q} \,\} \quad \text{and} \quad \mathfrak{Q} := \{\, \mathsf{q} \in \mathbb{R}^m \mid \boldsymbol{C}_{\mathsf{q}} \text{ contains more than 2 points} \,\}.$$

Clearly, we see that for solutions $\boldsymbol{c}(\cdot)$ of the RRE $c(0) \in \boldsymbol{C}_{\mathsf{q}}$ implies $\boldsymbol{c}(t) \in \boldsymbol{C}_{\mathsf{q}}$ for all $t > 0$, as long as the solution exists.

2.2 Complex and detailed balancing

The *complex-balancing condition* (CBC) asks that there is a positive state such that for all complexes $\mathcal{C}^l$ the inflow into the complex (see left-hand side below) and the outflow from the complex (see right-hand side below) are equal:

$$\text{(CBC)} \qquad \exists\, \boldsymbol{c}_* \in \mathbb{R}^I_> \;\forall\, l = 1,..,C: \quad \sum_{j=1}^{C} k_{jl} \boldsymbol{c}_*^{\boldsymbol{\alpha}^j} = \sum_{n=1}^{C} k_{ln} \boldsymbol{c}_*^{\boldsymbol{\alpha}^l}. \tag{2.3}$$

The *detailed-balance condition* (DBC) is stronger, since it assumes that all reactions are reversible, i.e. the number R of reactions is even with $R = 2N$, and, after a suitable reordering, the reaction $r' = n+N$ is the reverse reaction of reaction $r = n$, more precisely $S_{n+N} = P_n$ and $P_{n+N} = S_n$ for $n = 1,..,N = R/2$. The DBC now asks that there exists a positive equilibrium $\boldsymbol{c}_*$ such that each of the N reaction pairs is individually in balance:

$$\text{(DBC)} \qquad \exists\, \boldsymbol{c}_* \in \,]0,\infty[\; \forall\, n = 1,..,N = R/2: \;\; \kappa_n \boldsymbol{c}_*^{\boldsymbol{\alpha}^{S_n}} = \kappa_{n+N} \boldsymbol{c}_*^{\boldsymbol{\alpha}^{P_n}}. \tag{2.4}$$

In this case the RRE (2.1) takes the simpler form

$$\dot{\boldsymbol{c}} = \sum_{n=1}^{R/2} \widehat{\kappa}_n \Big(\frac{\boldsymbol{c}^{\boldsymbol{\alpha}^{S_n}}}{\boldsymbol{c}_*^{\boldsymbol{\alpha}^{S_n}}} - \frac{\boldsymbol{c}^{\boldsymbol{\alpha}^{P_n}}}{\boldsymbol{c}_*^{\boldsymbol{\alpha}^{P_n}}} \Big) \big(\boldsymbol{\alpha}^{P_n} - \boldsymbol{\alpha}^{S_n} \big) \quad \text{with } \widehat{\kappa}_n := \kappa_n \boldsymbol{c}_*^{\boldsymbol{\alpha}^{S_N}}. \tag{2.5}$$

To highlight the difference between these two concepts we follow [vSRJ15] and employ the graph-theoretic approach for the complex-based representation of the RRE, namely

$$\dot{\boldsymbol{c}} = ZDK\mathrm{Exp}\big(Z^\top \mathrm{Log}(\boldsymbol{c})\big), \tag{2.6}$$

where

$$\mathrm{Log}(\boldsymbol{c}) := \big(\log c_i\big)_{i=1,..,I} \quad \mathrm{Exp}(\boldsymbol{\zeta}) := \big(\mathrm{e}^{\zeta_r}\big)_{r=1,..,R}$$

and the matrices $Z \in \mathbb{R}^{I\times C}$, $D \in \mathbb{Z}^{C\times R}$ are $K \in \mathbb{R}^{R\times C}$ defined via

$$Z_{ij} = \alpha_i^j, \qquad D_{jr} = \begin{cases} 1 & \text{for } j = P_r, \\ -1 & \text{for } j = S_r, \\ 0 & \text{otherwise;} \end{cases} \qquad K_{rj} = \begin{cases} \kappa_r & \text{for } j = S_r, \\ 0 & \text{otherwise.} \end{cases}$$

In particular, we may define the matrix $L = -DK \in \mathbb{R}^{C\times C}$, which takes the form

$$L = \sum_{r=1}^{R} \kappa_r \Big(\boldsymbol{e}^C_{S_r} \otimes \boldsymbol{e}^C_{S_r} \;-\; \boldsymbol{e}^C_{P_r} \otimes \boldsymbol{e}^C_{S_r} \Big) \;\in \mathbb{R}^{C\times C},$$

where $\boldsymbol{e}_j^C$, $j = 1, .., C$, are the unit vectors in $\mathbb{R}^C$. Obviously, L satisfies

$$L_{jj} = \sum_{l=1}^{C} k_{jl} \geq 0, \quad L_{jl} = -k_{jl} \leq 0 \text{ for } l \neq j, \quad \text{and } \sum_{j=1}^{L} L_{jl} = 0 \text{ for all } l = 1, .., C. \tag{2.7}$$

Thus, we can interprete $-L$ as the generator of a Markov process on $\{1, ..., C\}$.

For a positive state $\boldsymbol{c}_*$ we can introduce the complex vector $\boldsymbol{\zeta}_* = \mathrm{Exp}\big(Z^\top \mathrm{Log}(\boldsymbol{c}_*)\big)$, then complex balancing can be characterized as follows:

$$\boldsymbol{c}_* \text{ satisfies (CBC)} \quad \Longleftrightarrow \quad L\,\boldsymbol{\zeta}_* = 0. \tag{2.8}$$

For a similar characterization of detailed balancing we assume $R = 2N$ and the numbering such that $S_{n+N} = P_n$ and $P_{n+N} = S_n$ for $n = 1, .., N = R/2$, which simply means

$$D = \big[\overline{D} \,\vdots\, -\overline{D}\big] \text{ with } D \in \mathbb{Z}^{C\times N} \quad \text{and} \quad K = \begin{bmatrix} K_{\mathrm{forw}} \\ K_{\mathrm{backw}} \end{bmatrix} \text{ with } K_{\mathrm{forw}}, K_{\mathrm{backw}} \in \mathbb{R}^{N\times C}.$$

Hence for a positive $\boldsymbol{c}_*$ with complex vector $\boldsymbol{\zeta}_* = \mathrm{Exp}\big(Z^\top \mathrm{Log}(\boldsymbol{c}_*)\big)$ we have

$$\text{(DBC)} \quad \Longleftrightarrow \quad K_{\mathrm{forw}}\boldsymbol{\zeta}_* = K_{\mathrm{backw}}\boldsymbol{\zeta}_*. \tag{2.9}$$

This shows that (DBC) implies (CBC) since $DK\boldsymbol{\zeta}_* = \overline{D}\big(K_{\mathrm{forw}} - K_{\mathrm{backw}}\big)\boldsymbol{\zeta}_* = 0$. However, the condition $\boldsymbol{\zeta}_* \in \mathrm{kernel}(K_{\mathrm{forw}} - K_{\mathrm{backw}})$ (typically N conditions) is generally stronger than $\boldsymbol{\zeta}_* \in \mathrm{kernel}(DK)$, since $\overline{D} \in \mathbb{Z}^{C\times N}$ may have a non-trivial kernel.

Example 2.1 (Linear reaction = Markov processes) *We consider a linear RRE* $\boldsymbol{c} = A\boldsymbol{c} \in \mathbb{R}^I$*, which can be written based on complexes by taking* $\mathcal{C}_j = \mathcal{A}_j$*. This gives* $Z = I$ *and* $\mathrm{Exp}\big(Z^\top \mathrm{Log}(\boldsymbol{c})\big) = \boldsymbol{c}$*. Moreover, we simply have* $L = -DK = -A$*.*

This leads us to the observation that every strictly positive equilibrium $\boldsymbol{c}_* \in \mathbb{R}^I_>$ *of the Kolmogorov equation* $\dot{\boldsymbol{c}} = A\boldsymbol{c} = -L\boldsymbol{c}$ *is already a complex-balanced equilibrium. Clearly, detailed balance needs the additional relations* $A_{ij}c_j^* = A_{ji}c_i^*$ *for all* $i, j = 1, .., I$*, which are not satisfied in general. Markov processes with detailed balance are usually called (microscopically) reversible Markov processes, see e.g. [MPR14].*

Example 2.2 (A case with deficiency 1) *We consider an example with two species* $\mathcal{A}_1$ *and* $\mathcal{A}_2$*, three complexes, and 6 reactions, namely*

$$\mathcal{C}_1 := 2\mathcal{A}_1 \underset{\kappa_2}{\overset{\kappa_1}{\rightleftharpoons}} \mathcal{C}_2 := 2\mathcal{A}_2 \underset{\kappa_4}{\overset{\kappa_3}{\rightleftharpoons}} \mathcal{C}_3 := \mathcal{A}_1 + \mathcal{A}_2 \underset{\kappa_6}{\overset{\kappa_5}{\rightleftharpoons}} \mathcal{C}_1 \tag{2.10}$$

All 6 reactions have a stoichiometric vector that is parallel to $(1, -1)^\top$*, and the RRE reads*

$$\begin{pmatrix} \dot{c}_1 \\ \dot{c}_2 \end{pmatrix} = \big(2\kappa_1 c_1^2 - 2\kappa_2 c_2^2 - \kappa_3 c_2^2 + \kappa_4 c_1 c_2 - \kappa_5 c_1 c_2 + \kappa_6 c_1^2\big) \begin{pmatrix} -1 \\ +1 \end{pmatrix}.$$

The deficiency δ *is obtained from the formula* $\delta = m - \ell - \dim \mathbb{S}$*, where* $m = 3$ *is the number of complexes,* $\ell = 1$ *is the number of connected components of the complex graph, and the stoichiometric subspace* $\mathbb{S}$ *has dimension 1. Hence, we conclude* $\delta = 1$*.*

The matrices Z and D in [vSRJ15] for $\dot{\boldsymbol{c}} = ZDK\mathrm{Exp}\big(Z^\top \mathrm{Log}(\boldsymbol{c})\big)$ are given via

$$Z=\begin{pmatrix}2&0&1\\0&2&1\end{pmatrix},\ D=\begin{pmatrix}-1&1&0&0&1&-1\\1&-1&-1&1&0&0\\0&0&1&-1&-1&1\end{pmatrix},\ K=\begin{pmatrix}\kappa_1&0&0\\0&\kappa_2&0\\0&\kappa_3&0\\0&0&\kappa_4\\0&0&\kappa_5\\\kappa_6&0&0\end{pmatrix},\ L=\begin{pmatrix}\kappa_1+\kappa_6&-\kappa_2&-\kappa_5\\-\kappa_1&\kappa_2+\kappa_3&-\kappa_4\\-\kappa_6&-\kappa_3&\kappa_4+\kappa_5\end{pmatrix}$$

if all $k_j > 0$, otherwise the corresponding columns in D and rows in K disappear. Clearly, we have $\mathrm{kernel}Z = \mathrm{span}(1,1,-2)^\top$ and thus $\mathrm{kernel}Z \subset \mathrm{im}D$, if at least two of the three values $\kappa_i+\kappa_{3+i}$, $i = 1,2,3$, are positive. This confirms $\delta = \dim\big(\ker Z \cap \mathrm{im}D\big) = 1$.

The system satisfies the detailed-balance condition if and only if the two Wegscheider conditions

$$\kappa_1\kappa_3^2 = \kappa_2\kappa_4^2 \text{ and } \kappa_4\kappa_5 = \kappa_3\kappa_6$$

hold. The exact conditions for the complex-balancing can be derived by the theory in [vSRJ15, Sec. 3], which leads to one transcendental relation for $(k_1,\dots,k_6)$.

We highlight the difference by considering the special case that $\boldsymbol{c}_* = (1,1)^\top$ is an equilibrium. Then, $\mathrm{Exp}\big(Z^\top\mathrm{Log}(\boldsymbol{c}_*)\big) = (1,1,1)^\top$. Defining the three relations

$$(\mathrm{R}_1)\ 2\kappa_1+\kappa_4+\kappa_6 = 2\kappa_2+\kappa_3+\kappa_5,\quad (\mathrm{R}_2)\ \kappa_3+\kappa_6 = \kappa_4+\kappa_5,\quad (\mathrm{R}_3)\ \kappa_3 = \kappa_4,$$

we obtain the following conditions for the different balancing conditions:

(A) $\boldsymbol{c}_* = (1,1)^\top$ is an equilibrium if and only if (R_1) holds.

(B) $\boldsymbol{c}_* = (1,1)^\top$ is a complex-balanced equilibrium if and only if (R_1) and (R_2) hold.

(C) $\boldsymbol{c}_* = (1,1)^\top$ is a detailed-balanced equilibrium if and only if (R_1)–(R_3) hold.

*Another important case of deficiency-1 systems arises in semiconductor physics, see [MP*16], where the three species are electrons, holes, and photons. The first reaction pair is spontaneous emission and recombination, namely $X_{el} + X_{ho} \rightleftharpoons X_{ph}$; while the second reaction pair is optical generation, namely $X_{el}+X_{ho}+X_{ph} \rightleftharpoons 2X_{ph}$, such that both vectors $\boldsymbol{\gamma}^r = \boldsymbol{\alpha}^r-\boldsymbol{\beta}^r = (1,1,-1)$. We have $m = 4$ complexes, $\ell = 2$ connected components, and $\dim\mathbb{S} = 1$, hence $\delta = 1$. In this system complex balance and detailed balance coincide.*

2.3 Decay of relative entropy

We now discuss the decay of the relative entropy. First we give a short, self-contained proof of the fact that for every complex-balanced RRE equation the relative entropy $\boldsymbol{c} \mapsto H(\boldsymbol{c}|\boldsymbol{c}_*)$ is a Liapunov function. This result was first obtained already in [HoJ72, Thm. 6A]. The main ideas is to transfer the well-known decay result for the relative entropy for linear Markov processes of the form $\dot{\boldsymbol{\zeta}} = -L\boldsymbol{\zeta}$ from the level of complexes to the concentrations $\boldsymbol{c}$ by exploiting the representation $\dot{\boldsymbol{c}} = \boldsymbol{R}(\boldsymbol{c}) = Z(-L)\mathrm{Exp}\big(Z^\top\mathrm{Log}(\boldsymbol{c})\big)$.

Proposition 2.3 (Complex balancing and relative entropy) *Consider a RRE $\dot{\boldsymbol{c}} = \boldsymbol{R}(\boldsymbol{c})$ of mass-action type with an equilibrium $\boldsymbol{c}_* \in \mathbb{R}^I_>$ satisfying the complex-balance condition (CBC), see (2.3). Then, the relative entropy*

$$F(\boldsymbol{c}) = H(\boldsymbol{c}|\boldsymbol{c}_*) = \sum_{i=1}^I c_i^*\lambda_{\mathrm{B}}\big(c_i/c_i^*\big) \quad \text{with } \lambda_{\mathrm{B}}(z) = z\log z - z + 1$$

is a Liapunov function, i.e. $\boldsymbol{R}(\boldsymbol{c})\cdot \mathrm{D}F(\boldsymbol{c})\le 0$ *for all* $\boldsymbol{c}\in\mathbb{R}^I_>$.

Proof. Using the relation $\boldsymbol{R}(\boldsymbol{c}) = -ZL\,\mathrm{Exp}\big(Z^\top \mathrm{Log}(\boldsymbol{c})\big)$, we obtain the identity

$$-\boldsymbol{R}(\boldsymbol{c})\cdot \mathrm{D}F(\boldsymbol{c}) = L\,\mathrm{Exp}\big(Z^\top\mathrm{Log}(\boldsymbol{c})\big)\cdot\Big(Z^\top\mathrm{Log}(\boldsymbol{c}) - Z^\top\mathrm{Log}(\boldsymbol{c}_*)\Big).$$

We introduce $\boldsymbol{\zeta} = \mathrm{Exp}\big(Z^\top\mathrm{Log}(\boldsymbol{c})\big)$ and $\boldsymbol{\zeta}_* = \mathrm{Exp}\big(Z^\top\mathrm{Log}(\boldsymbol{c}_*)\big)$ lying in $\mathbb{R}^C_>$ and satisfying $L\boldsymbol{\zeta}_* = 0$ because of the CBC, see (2.8). Setting $G(\boldsymbol{\zeta}) = \sum_{j=1}^C \zeta_j^*\lambda_{\mathrm{B}}\big(\zeta_j/\zeta_j^*\big)$ we find

$$-\boldsymbol{R}(\boldsymbol{c})\cdot \mathrm{D}F(\boldsymbol{c}) = L\boldsymbol{\zeta}\cdot \mathrm{D}G(\boldsymbol{\zeta}). \tag{2.11}$$

Since $-L\in\mathbb{R}^{C\times C}$ is the generator of a Markov process, cf. (2.7), there is a $t_1>0$ such that $S^t := I - tL \in \mathbb{R}^{C\times C}_\ge$ for all $t\in\,]0,t_1[$, i.e. all entries are non-negative and $\sum_{j=1}^C S^t_{jl} = 1$ for all l. Note that G is again a relative entropy in the form

$$G(\boldsymbol{\zeta}) = H(\boldsymbol{\zeta}|\boldsymbol{\zeta}_*) := \sum_{j=1}^C h(\zeta_j,\zeta_j^*) \quad \text{with } h(a,b) = a\log a - a\log b - a + b.$$

Since $(a,b)\mapsto h(a,b)$ is convex and 1-homogeneous on $\mathbb{R}^2_\ge$, we can apply Jensen's inequality for the probability distribution $\big(\frac{1}{\sigma_j}S_{jl}\big)_{l=1,..,C}$ with $\sigma_l = \sum_{l=1}^C S_{jl}$ to obtain

$$\begin{aligned} h\big((S^t\boldsymbol{\zeta})_j,(S^t\boldsymbol{\xi})_j\big) = h\Big(\sum_1^C S^t_{jl}\big(\zeta_l,\xi_l\big)\Big) &\overset{\text{1-hom}}{=} \sigma_j\, h\Big(\sum_1^C \frac{S^t_{jl}}{\sigma_j}\big(\zeta_l,\xi_l\big)\Big)\\ &\overset{\text{Jensen}}{\le} \sigma_j\sum_{l=1}^C \frac{S^t_{jl}}{\sigma_j}h\big(\zeta_l,\xi_l\big) = \sum_{l=1}^C S^t_{jl}h\big(\zeta_l,\xi_l\big).\end{aligned}$$

Adding over $j=1,..,C$ we can use $\sum_{j=1}^l S_{jl}=1$ for all l and find $H(S^t\boldsymbol{\zeta}|S^t\boldsymbol{\xi})\le H(\boldsymbol{\zeta}|\boldsymbol{\xi})$. With $S^t\boldsymbol{\zeta}_* = \boldsymbol{\zeta}_*$ we conclude

$$G(S^t\boldsymbol{\zeta}) = H(S^t\boldsymbol{\zeta}|\boldsymbol{\zeta}_*) = H(S^t\boldsymbol{\zeta}|S^t\boldsymbol{\zeta}_*)\le H(\boldsymbol{\zeta}|\boldsymbol{\zeta}_*) = G(\boldsymbol{\zeta}).$$

Hence, we have $\frac{1}{t}\big(G(\boldsymbol{\zeta})-G(S^t\boldsymbol{\zeta})\big)\ge 0$ for all $t\in\,]0,t_1]$. Now $\frac{1}{t}(S^t-I)\to -L$ yields

$$0\le \lim_{t\searrow 0}\frac{1}{t}\big(G(\boldsymbol{\zeta})-G(S^t\boldsymbol{\zeta})\big) = \mathrm{D}G(\boldsymbol{\zeta})\cdot L\boldsymbol{\zeta},$$

which gives the desired result after exploiting (2.11). ∎

Note that in the above result the equilibrium $\boldsymbol{c}_*$ does not have to lie in the same stoichiometric compatibility class $\boldsymbol{C}_\mathsf{q}$ as the solution. However, on each $\boldsymbol{C}_\mathsf{q}$ the strictly convex and coercive functional $\boldsymbol{c}\mapsto H(\boldsymbol{c}|\boldsymbol{c}_*)$ attains its unique minimizer and we set

$$\boldsymbol{w}_\mathsf{q} := \mathrm{argmin}\{\, H(\boldsymbol{c}|\boldsymbol{c}_*)\mid \boldsymbol{c}\in\boldsymbol{C}_\mathsf{q}\,\}.$$

By La Salle's principle, $\boldsymbol{w}_\mathsf{q}$ is an equilibrium, i.e. $\boldsymbol{R}(\boldsymbol{w}_\mathsf{q})=0$. Vice versa any equilibrium of $\boldsymbol{c}=\boldsymbol{R}(\boldsymbol{c})$ must be a stationary point of $H(\,\cdot\,|\boldsymbol{c}_*)$ on $\boldsymbol{C}_\mathsf{q}$, so it must coincide with $\boldsymbol{w}_\mathsf{q}$ unless it is a boundary equilibrium. The minimizer property of $\boldsymbol{w}_\mathsf{q}$ implies that

$$\mathrm{D}_{\boldsymbol{c}}H(\boldsymbol{w}_\mathsf{q}|\boldsymbol{c}_*) = \Big(\log\big(w_i^\mathsf{q}/\boldsymbol{c}_i^*\big)\Big)_{i=1,..,I} =: \boldsymbol{t}(\boldsymbol{c}_*,\boldsymbol{w}_\mathsf{q})\in\mathbb{S}^\perp,$$

and, using (2.2) we find the explicit representation of all positive equilibria, viz.

$$\boldsymbol{w}_{\mathsf{q}} = \operatorname{diag}\big(\mathsf{Q}^\top \mu_{\mathsf{q}}\big)\, \boldsymbol{c}_* \text{ for some } \mu_{\mathsf{q}} \in \mathbb{R}^m. \tag{2.12}$$

¿From this we easily see that $\boldsymbol{c} \mapsto H(\boldsymbol{c}|\boldsymbol{w}_{\mathsf{q}})$ is a Liapunov function as well. Indeed, using

$$H(\boldsymbol{c}|\boldsymbol{w}_{\mathsf{q}}) = H(\boldsymbol{c}|\boldsymbol{c}_*) + \boldsymbol{c}\cdot \boldsymbol{t}(\boldsymbol{c}_*, \boldsymbol{w}_{\mathsf{q}}) + \big(\boldsymbol{w}_{\mathsf{q}} - \boldsymbol{c}_*\big)\big)\cdot (1,..,1)^\top$$

implies that $\frac{\mathrm{d}}{\mathrm{d}t} H(\boldsymbol{c}(t)|\boldsymbol{w}_{\mathsf{q}}) = \frac{\mathrm{d}}{\mathrm{d}t} H(\boldsymbol{c}(t)|\boldsymbol{c}_*)$ along solutions of the RRE.

Moreover, defining $\boldsymbol{\zeta}_{\mathsf{q}} = \operatorname{Exp}\big(Z^\top \operatorname{Log}(\boldsymbol{w}_{\mathsf{q}})\big)$ gives

$$\boldsymbol{\zeta}_{\mathsf{q}} = \operatorname{Exp}\Big(Z^\top \big(\operatorname{Log}(\boldsymbol{c}_*) + \boldsymbol{t}(\boldsymbol{c}_*, \boldsymbol{w}_{\mathsf{q}})\big)\Big) = \operatorname{Exp}\big(Z^\top \operatorname{Log}(\boldsymbol{c}_*)\big) =: \boldsymbol{\zeta}_*,$$

because $\boldsymbol{t}(\boldsymbol{c}_*, \boldsymbol{w}_{\mathsf{q}}) \in \mathbb{S}^\perp$ implies $Z^\top \boldsymbol{t}(\boldsymbol{c}_*, \boldsymbol{w}_{\mathsf{q}}) = 0$. Thus, we have $L\boldsymbol{\zeta}_q = L\boldsymbol{\zeta}_* = 0$, which means that $\boldsymbol{w}_{\mathsf{q}}$ also satisfies the CBC. This fact was already established in [Fei73].

For a quantitative decay argument we now assume that in each $\boldsymbol{C}_{\mathsf{q}}$ there is exactly one equilibrium, namely the *unique equilibrium condition* (UEC):

$$\text{(UEC)} \qquad \forall\, \mathsf{q} \in \mathfrak{Q}: \quad \{\, \boldsymbol{c} \in \boldsymbol{C}_{\mathsf{q}} \mid \boldsymbol{R}(\boldsymbol{c}) = 0 \,\} = \{\boldsymbol{w}_{\mathsf{q}}\}, \tag{2.13}$$

which follows e.g. from the assumptions that for all reactions we have $\alpha_i^{S_r}\alpha_i^{P_r} = 0$ for $i = 1,..,I$ (no autocatalytic species).

Now we can define the dissipation

$$D_{\mathrm{R}}(\boldsymbol{c}) := \boldsymbol{R}(\boldsymbol{c}) \cdot \mathrm{D}_{\boldsymbol{c}} H(\boldsymbol{c}|\boldsymbol{c}_*) = \boldsymbol{R}(\boldsymbol{c}) \cdot \big(\log(c_i/c_i^*)\big)_{i=1,..,I}$$

and note that in the above arguments we may replace $\boldsymbol{c}_*$ by any $\boldsymbol{w}_{\mathsf{q}}$, without changing the value of D_{R}. For the RRE we now define an energy-dissipation estimate depending on $\mathsf{q} \in \mathfrak{Q}$. By $k_{\mathrm{R}}(\mathsf{q}) \geq 0$ we denote the largest value such that the estimate

$$\forall\, \boldsymbol{c} \in \boldsymbol{C}_{\mathsf{q}}: \quad D_{\mathrm{R}}(\boldsymbol{c}) \geq k_{\mathrm{R}}(\boldsymbol{q}) H(\boldsymbol{c}|\boldsymbol{w}_{\mathsf{q}}) \tag{2.14}$$

holds. Further on, we are only interested in the case $k_{\mathrm{R}}(\mathsf{q}) > 0$, which is easy to show if $\boldsymbol{C}_{\mathsf{q}}$ is compact, e.g. it is an implicit consequence of our compact argument in Section 4, see also [GlH97, MHM15]. We do not know whether positivity of $k_{\mathrm{R}}(\mathsf{q})$ also holds for non-compact $\boldsymbol{C}_{\mathsf{q}}$.

Of course, (2.14) provides a uniform quantitative decay estimate for $\boldsymbol{c}(t)$ to the solutions namely

$$\boldsymbol{c}(0) \in \boldsymbol{C}_{\mathsf{q}} \iff H(\boldsymbol{c}(t)|\boldsymbol{w}_{\mathsf{q}}) \leq \exp\big(-k_{\mathrm{R}}(\mathsf{q})t\big) H(\boldsymbol{c}(0)|\boldsymbol{w}_{\mathsf{q}}) \text{ for all } t > 0.$$

¿From the lower estimate $\lambda_{\mathrm{B}}(z) \geq 4(\sqrt{z}-1)^2$ we obtain $H(\boldsymbol{c}|\boldsymbol{w}) \geq 4\sum_{i=1}^I \big(\sqrt{c_i} - \sqrt{w_i}\big)^2$, and the convergence of $|\boldsymbol{c}(t) - \boldsymbol{w}_{\mathsf{q}}| \leq C \exp\big(-k_{\mathrm{R}}(\mathsf{q})t/2\big)$ follows.

3 Constructive methods

3.1 Basic observations for RDS

We now want to discuss some of the recently developed methods to show similar decay estimates for RDS of the form

$$\dot{\boldsymbol{c}} = \operatorname{diag}(\delta_1, ..., \delta_I)\Delta \boldsymbol{c} + \boldsymbol{R}(\boldsymbol{c}) \text{ in } \Omega, \quad \nu \cdot \nabla \boldsymbol{c} = 0 \text{ on } \partial\Omega. \tag{3.1}$$

Having identified a Liapunov function $H_{\mathsf{q}}(\boldsymbol{c}) = H(\boldsymbol{c}|\boldsymbol{w}_{\mathsf{q}})$ for the RRE we can use the argument in [Ali79] to define a Liapunov functional $\mathcal{H}_{\mathsf{q}}$ for the RDS as well. For this we note that the conserved quantities q still exist, but now in an averaged sense. Recalling $|\Omega| = 1$ we define

$$\overline{\boldsymbol{c}} = \int_\Omega \boldsymbol{c}(x)\,\mathrm{d}x, \quad \mathcal{Q}\boldsymbol{c} = \int_\Omega \mathsf{Q}\boldsymbol{c}(x)\,\mathrm{d}x = \mathsf{Q}\overline{\boldsymbol{c}}.$$

Then, using the no-flux boundary conditions in (3.1) we easily obtain $\mathcal{Q}\boldsymbol{c}(t) = \boldsymbol{Q}\boldsymbol{c}(0)$ for all $t > 0$. Thus, for $\mathsf{q} \in \mathfrak{Q}$ we define the sets

$$\mathfrak{S}(\mathsf{q}) := \left\{ \boldsymbol{c} \in \mathrm{L}^1(\Omega)^I \;\middle|\; \boldsymbol{c}(x) \in [0,\infty[^I \text{ a.e. in } \Omega,\ \mathcal{Q}\boldsymbol{c} = \mathsf{q} \right\}$$

and the adjusted Liapunov functions

$$\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}) := \int_\Omega H(\boldsymbol{c}(x)|\boldsymbol{w}_{\mathsf{q}})\,\mathrm{d}x.$$

Obviously, $\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}) \geq 0$ for all $\boldsymbol{c}$ with equality if and only if $\boldsymbol{c} \equiv \boldsymbol{w}_{\mathsf{q}} \in \mathfrak{S}(\mathsf{q})$. Taking another $\widetilde{\mathsf{q}} \in \mathfrak{Q}$, then for $\boldsymbol{c} \in \mathfrak{S}(\mathsf{q})$ we have $\mathcal{H}_{\widetilde{\mathsf{q}}}(\boldsymbol{c}) = \mathcal{H}_{\mathsf{q}}(\boldsymbol{c}) + \mathcal{H}_{\widetilde{\mathsf{q}}}(\boldsymbol{w}_{\mathsf{q}})$, which implies that all functionals $\mathcal{H}_{\mathsf{q}}$ are Liapunov functions for (3.1) independent of $\widetilde{\mathsf{q}} = \mathcal{Q}\boldsymbol{c}(0)$. However, only in the case $\mathsf{q} = \widetilde{\mathsf{q}}$ we have the chance to show exponential decay of $\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}(t))$.

The dissipation generated by (3.1) and $\mathcal{H}_{\boldsymbol{q}}$ is given by

$$\mathcal{D}(\boldsymbol{c}) = \frac{\mathrm{d}}{\mathrm{d}}\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}) = \mathcal{D}_{\mathrm{D}}(\boldsymbol{c}) + \mathcal{D}_{\mathrm{R}}(\boldsymbol{c}),$$
$$\text{where } \mathcal{D}_{\mathrm{D}}(\boldsymbol{c}) = \int_\Omega \sum_{i=1}^I \delta_i \frac{|\nabla c_i|^2}{c_i}\,\mathrm{d}x \quad \text{and} \quad \mathcal{D}_{\mathrm{R}}(\boldsymbol{c}) = \int_\Omega D_{\mathrm{R}}(\boldsymbol{c}(x))\,\mathrm{d}x.$$

As in the case of the RRE the dissipation for $\mathcal{H}_{\mathsf{q}}$ does not depend on the value of q. Nevertheless the decay of $\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}(t))$ may depend on $\mathsf{q} = \mathcal{Q}\boldsymbol{c}(0)$, since the solutions are confined to stay in $\mathfrak{S}(\mathsf{q})$.

The aim of this paper is to establish energy-dissipation estimate in the form

$$\forall\, \mathsf{q} \in \mathfrak{Q}\ \exists\, K(\mathsf{q}) > 0\ \forall\, \boldsymbol{c} \in \mathfrak{S}(\mathsf{q}): \quad \mathcal{D}(\boldsymbol{c}) \geq K(\mathsf{q})\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}). \tag{3.2}$$

We see that the two dissipative parts $\mathcal{D}_{\mathrm{D}}$ and $\mathcal{D}_{\mathrm{R}}$ have to interact to generate the desired estimate. The diffusion part $\mathcal{D}_{\mathrm{D}}$ controls the deviation of each individual c_i from its mean value $\overline{c}_i$, but generates not interaction between the species. The reactive part $\mathcal{D}_{\mathrm{R}}$ controls at a fixed point $x \in \Omega$ the distance of $\boldsymbol{c}(x)$ from the set of equilibria of $\boldsymbol{R}(\boldsymbol{c})$.

3.2 The convexity method

For scalar drift-diffusion equations the log-Sobolev inequality plays a crucial role. For our bounded, Lipschitz domain $\Omega \subset \mathbb{R}^d$ we denote by $\rho_{\mathrm{lSo}}(\Omega)$ the largest constant such that

$$\forall\, u \in \mathrm{W}^{1,\infty}(\Omega): \quad \int_\Omega \frac{|\nabla u(x)|^2}{u(x)}\,\mathrm{d}x \geq \rho_{\mathrm{lSo}}(\Omega)\overline{u} \int_\Omega \lambda_{\mathrm{B}}\big(u(x)/\overline{u}\big)\,\mathrm{d}x = \rho_{\mathrm{lSo}}\mathcal{H}(u|\overline{u}).$$

Further on, we will drop the argument Ω in the log-Sobolev constant $\rho_{\mathrm{lSo}}(\Omega)$ for notational convenience. The major result of the convexity method is given in the following theorem. It relies on the first simple observation that

$$\mathcal{D}_{\mathrm{R}}(\boldsymbol{c}) = \int_\Omega \sum_{i=1}^I \delta_i \frac{|\nabla c_i|^2}{c_i}\,\mathrm{d}x \geq \rho_{\mathrm{lSo}} \int_\Omega \sum_{i=1}^I \delta_i H(c_i(x)|\overline{c}_i)\,\mathrm{d}x \geq \rho_{\mathrm{lSo}}\delta_{\min}\mathcal{H}(\boldsymbol{c}|\overline{\boldsymbol{c}}), \tag{3.3}$$

where $\delta_{\min} = \min\{\,\delta_I \mid i = 1, .., I\,\}$. Second we use that for $\boldsymbol{c} \in \mathfrak{S}(\mathsf{q})$ we have the relation

$$\mathcal{H}(\boldsymbol{c}|\overline{\boldsymbol{c}}) = \mathcal{H}(\boldsymbol{c}|\boldsymbol{w}_{\mathsf{q}}) - \mathcal{H}(\overline{\boldsymbol{c}}|\boldsymbol{w}_{\mathsf{q}}) = \mathcal{H}_{\mathsf{q}}(\boldsymbol{c}) - H_{\mathsf{q}}(\overline{\boldsymbol{c}}), \tag{3.4}$$

where we use the definitions $H_{\mathsf{q}}(\boldsymbol{c}) := H(\boldsymbol{c}|\boldsymbol{w}_{\mathsf{q}})$ and $\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}) := \mathcal{H}(\boldsymbol{c}|\boldsymbol{w}_{\mathsf{q}})$. Obviously, the negative term $H_{\mathsf{q}}(\overline{\boldsymbol{c}})$ must be controlled by the reactive dissipation as in (2.14). However, the major point is to relate the pointwise reactive dissipation $D_{\mathrm{R}}(\boldsymbol{c}(x))$ with that of the average, namely $D_{\mathrm{R}}(\overline{\boldsymbol{c}})$. Following [MHM15] a suitable control of the difference between $\mathcal{D}_{\mathrm{R}}(\boldsymbol{c}) = \overline{D_{\mathrm{R}}(\boldsymbol{c})}$ and $D_{\mathrm{R}}(\overline{\boldsymbol{c}})$ can be obtained through a convexity assumption exploiting the strict convexity of $\boldsymbol{c} \mapsto H(\boldsymbol{c}|\boldsymbol{w}_{\mathsf{q}})$. In the following condition (3.5) we generalize the condition in [MHM15, Thm. 3.1], where only the case $\mu_1 = .. = \mu_I = \mu$ is considered.

Theorem 3.1 (Convexity method) *Consider the setting of equation* (3.1) *with the Liapunov functionals* $\mathcal{H}_{\mathsf{q}}$ *and the dissipation* $\mathcal{D} = \mathcal{D}_{\mathrm{D}} + \mathcal{D}_{\mathrm{R}}$*, where the pointwise dissipation* D_{R} *satisfies* (2.14)*. Assume further that*

$$\exists\, \mu_1, ..., \mu_I \geq 0: \quad \boldsymbol{c} \mapsto D_{\mathrm{R}}(\boldsymbol{c}) + \sum_{i=1}^I \mu_i \lambda_{\mathrm{B}}(c_i) \quad \text{is convex}, \tag{3.5}$$

then we have the energy-dissipation estimate (3.2) *with*

$$K(\mathsf{q}) \geq \min\Big\{\, k_{\mathrm{R}}(\mathsf{q})\,,\, \rho_{\mathrm{lSo}}\delta_i \frac{k_{\mathrm{R}}(\mathsf{q})}{\mu_i + k_{\mathrm{R}}(\mathsf{q})} \;\Big|\; i = 1, \dots, I \,\Big\}. \tag{3.6}$$

Proof. For each i we set $r_i = \delta_i \rho_{\mathrm{lSo}}(\Omega) > 0$ and choose $\theta \in]0, 1[$. Then, for all $\boldsymbol{c} \in \mathfrak{S}(\mathsf{q})$, we have the estimate

$$\begin{aligned}
\mathcal{D}(\boldsymbol{c}) &\geq \int_\Omega \Big(D_{\mathrm{R}}(\boldsymbol{c}(x)) + \sum_{i=1}^I H(c_i(x)|\overline{c}_i) \Big)\,\mathrm{d}x \\
&= \int_\Omega \Big(D_{\mathrm{R}}(\boldsymbol{c}(x)) + \sum_{i=1}^I \theta_i r_i H(c_i(x)|\overline{c}_i) \;+\; \sum_{j=1}^I (1-\theta_j) r_i H(c_i(x)|\overline{c}_j) \Big)\,\mathrm{d}x \\
&\geq \Theta_{\mathrm{R}} \int_\Omega \Big(D_{\mathrm{R}}(\boldsymbol{c}(x)) + \sum_{i=1}^I \mu_i H(c_i(x)|\overline{c}_i) \Big)\,\mathrm{d}x \;+\; \Theta_{\mathrm{D}} \mathcal{H}(\boldsymbol{c}(\cdot)|\overline{\boldsymbol{c}}),
\end{aligned}$$

where $\Theta_R := \min\big\{\, 1\,,\, \theta_i r_i/\mu_i \;\big|\; i = 1, .., I\,\big\}$ and $\Theta_{\mathrm{D}} := \min\big\{\, (1-\theta_j) r_j \;\big|\; j = 1, .., I\,\big\}$.

For the first term we use the convexity (3.5) and Jensen's inequality, and for the second we use $\boldsymbol{c} \in \mathfrak{S}(\mathsf{q})$ and (3.4):

$$\begin{aligned}
&\geq \Theta_R \int_\Omega \big(\mu H(\overline{\boldsymbol{c}}|\overline{\boldsymbol{c}}) + D_{\mathrm{R}}(\overline{\boldsymbol{c}}) \big)\,\mathrm{d}x + \Theta_{\mathrm{D}} \big(\mathcal{H}(\boldsymbol{c}|\boldsymbol{w}_{\mathsf{q}}) - \mathcal{H}(\overline{\boldsymbol{c}}|\boldsymbol{w}_{\mathsf{q}}) \big) \\
&\underset{\mathsf{Q}\overline{\boldsymbol{c}}=\mathsf{q}}{\geq^{(2.14)}} \Theta_R k_{\mathrm{R}}(\mathsf{q}) H_{\mathsf{q}}(\overline{\boldsymbol{c}}) + \Theta_{\mathrm{D}} \big(\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}) - H_{\mathsf{q}}(\overline{\boldsymbol{c}}) \big) \;\geq\; \min\big\{ \Theta_R, \Theta_{\mathrm{D}} \big\}\, \mathcal{H}_{\mathsf{q}}(\boldsymbol{c}).
\end{aligned}$$

Using the optimal $\theta_i = \mu_i/(\mu_i+k_{\mathrm{R}}(\mathsf{q}))$ the desired estimate (3.2) with $K(\mathsf{q})$ satisfying (3.6) is established. ∎

We emphasize that the convexity method described above does not depend on the condition of detailed balance as used in [MHM15], but only used the reactive dissipation $D_{\mathrm{R}}(\boldsymbol{c})$ which has to be non-negative, satisfy the estimate (2.14), and must be convexifiable by adding $\mu H(\boldsymbol{c}|\boldsymbol{c}_*)$. Thus, it is ideally suited to handle the case of complex-balanced reaction systems as well.

Of course, the above theorem is only the simplest form of the convexity method. We refer to [MHM15] for generalizations involving more general relative entropies or cases where $\delta_i = 0$ for some i. In [HH*16, MiM16] it is also shown that the method can be adapted to the case of energy-reaction-diffusion systems where the equilibrium state $\boldsymbol{c}_* = \boldsymbol{w}(u)$ may depend on the internal energy $u \in [0,\infty[$.

Example 3.2 (Explicit bounds for $\mathcal{A}_1 \rightleftharpoons 2\mathcal{A}_2$) *To highlight the usability of the approach we consider the system*

$$\dot c_1 = \operatorname{div}\big(\delta_1\nabla c_1\big) + \kappa(c_2^2 - c_1), \qquad \dot c_2 = \operatorname{div}\big(\delta_2\nabla c_2\big) + 2\kappa(c_1 - c_2^2), \tag{3.7}$$

for which we have $\mathsf{Q}\overline{\boldsymbol{c}} = 2\overline{c}_1 + \overline{c}_2$ and $\boldsymbol{c}_* = (1,1)^\top$. The reactive part of the dissipation is $D_{\mathrm{R}}(\boldsymbol{c}) = \kappa(c_2^2 - c_1)\log\big(c_2^2/c_1\big)$, which is clearly nonconvex, since $D_{\mathrm{R}}(\boldsymbol{c}) = 0$ if and only if $c_1 = c_2^2$. It was shown in [MHM15, Lem. 4.3] that the function

$$\boldsymbol{c} \mapsto \mu_1 H(c_1|1) + D_{\mathrm{R}}(c_1, c_2)$$

is convex for $\mu_1 \geq \kappa\mu_*$ with $\mu_* \approx 1.1675$. Based on this, and an analysis of the RRE it is shown that (3.2) holds with

$$K(\mathsf{q}) \geq \min\big\{\frac{1}{4}\delta_1\rho_{\mathrm{lSo}}(\Omega), \delta_2\rho_{\mathrm{lSo}}(\Omega), \frac{2}{5}\kappa\big\}.$$

Moreover, it could be shown that a suitable generalization of the convexity method allows one to handle the case $\delta_2 = 0$ as well leading to a lower estimate of the form

$$K(\mathsf{q}) \geq \min\{\delta_1\rho_{\mathrm{lSo}}(\Omega), 2\kappa\}\min\big\{\frac{\mathsf{q}}{10}, \frac{7}{100}\big\}.$$

3.3 Applicability of convexity method for $a\mathcal{A}_1 \rightleftharpoons b\mathcal{A}_2$

Here we investigate the question to which two-species models with reaction pair $a\mathcal{A}_1 \rightleftharpoons b\mathcal{A}_2$ the convexity method can be applied. The RDS reads

$$\dot c_1 = \delta_1\Delta c_1 + \kappa a\big(c_2^b - c_1^a\big),\ \dot c_2 = \delta_2\Delta c_2 + \kappa b\big(c_1^a - c_2^b\big) \text{ in } \Omega, \quad \nu\cdot\nabla c_j = 0 \text{ on } \partial\Omega. \tag{3.8}$$

Here $\delta_i, \kappa > 0$ and the stoichiometric coefficients satisfy $a, b \geq 1$. The stoichiometric subspace is $\mathbb{S} = \operatorname{span}(-a, b)^\top$, and $\mathsf{Q} \in \mathbb{R}^{1\times 2}$ is given via $\mathsf{Q}\boldsymbol{c} = bc_1 + ac_2$,

The RRE reads $\dot{\boldsymbol{c}} = -(c_1^a - c_2^b)\,(a,-b)^\top$, and we need convexity of

$$G_{\boldsymbol{\mu}}(c_1,c_2) := \mu_1\lambda_{\mathrm{B}}(c_1) + \mu_2\lambda_{\mathrm{B}}(c_2) + D_{\mathrm{R}}(c_1,c_2) \ \text{ with } D_{\mathrm{R}}(c_1,c_2) = (c_1^a - c_2^b)\log(c_1^a/c_2^b)$$

for some $\mu_1, \mu_2 \geq 0$. Here and in the sequel we often set $\kappa = 1$, but recover the obvious position of κ in the final result.

For joint convexity in both variables it is necessary to have separate convexity, namely that of $G_{\boldsymbol{\mu}}(\cdot, c_2)$ and $G_{\boldsymbol{\mu}}(c_1, \cdot)$ for all c_2 and c_1, respectively. Taking the second derivative of $G_{\boldsymbol{\mu}}(\cdot, c_2)$ we have to show that the infimum for $c_1, c_2 > 0$ is non-negative for some μ_1. From the explicit form

$$\partial_{c_1}^2 G_{\boldsymbol{\mu}}(c_1, c_2) = \frac{a}{c_1}\Big(\frac{\mu_1}{a} + \frac{c_2^b}{c_1} + c_1^{a-1}\big(2a{-}1{+}(a{-}1)\log(c_1^a/c_2^b)\big)\Big)$$

we see that the infimum is $-\infty$ for $a < 1$, by fixing $c_1 > 0$ and considering $c_2 \searrow 0$. For $a \geq 1$, we can minimize first with respect to c_2, which is attained for $c_2^b = (a{-}1)c_1^a$. Thus, for $a \geq 1$ we have

$$\min_{c_2>0} \partial_{c_1}^2 G_{\boldsymbol{\mu}}(c_1, c_2) = \frac{a}{c_1}\big(\mu_1 + f(a)c_1^{a-1}\big) \quad \text{with } f(a) := 3a{-}2{-}(a{-}1)\log(a{-}1).$$

For $a \in [1, m^*]$ with $m^* \approx 22.06217$ we have $f(a) \geq 0$ such that the term is non-negative for all $\mu_1 \geq 0$, while for $a > m^*$ the infimum over $c_1 > 0$ is $-\infty$. In summary, we conclude that $G_{\boldsymbol{\mu}}$ is separately convex if and only if $D_{\mathrm{R}}(c_1, c_2)$ is so, and this is the case if and only if $a, b \in [1, m^*]$, i.e. μ_1 and μ_2 cannot help for separate convexity.

It remains to find the subset where joint convexity holds. Using the diagonal matrix $K(\boldsymbol{c}) := \operatorname{diag}\big((c_1/a)^{1/2}, (c_2/b)^{1/2}\big)$ the Hessian gives

$$K(\boldsymbol{c})\mathrm{D}^2 G_{\boldsymbol{\mu}}(\boldsymbol{c})K(\boldsymbol{c}) = \begin{pmatrix} \frac{\mu_1}{a} & 0 \\ 0 & \frac{\mu_2}{b} \end{pmatrix} + L(\boldsymbol{c}) \text{ with}$$

$$L(\boldsymbol{c}) := \begin{pmatrix} \frac{c_2^b}{c_1} + c_1^{a-1}\big(2a{-}1{+}(a{-}1)\log\frac{c_1^a}{c_2^b}\big) & -\big(\frac{ab}{c_1c_2}\big)^{1/2}\big(c_1^a{+}c_2^b\big) \\ -\big(\frac{ab}{c_1c_2}\big)^{1/2}\big(c_1^a{+}c_2^b\big) & \frac{c_1^a}{c_2} + c_2^{b-1}\big(2b{-}1{+}(b{-}1)\log\frac{c_2^b}{c_1^a}\big) \end{pmatrix}$$

Thus, the existence of $\boldsymbol{\mu} = (\mu_1, \mu_2)$ such that $G_{\boldsymbol{\mu}}(\cdot)$ is (jointly) convex, is equivalent to showing that the eigenvalues of $L(\boldsymbol{c})$ are bounded from below uniformly for $c_1, c_2 > 0$. By our restriction $a, b \in [1, m^*]$ we know that the diagonal terms are non-negative.

For $a = b = 1$ we obviously have $L(\boldsymbol{c}) \geq 0$, which is the convexity of $\boldsymbol{c} \mapsto (c_1{-}c_2)\log(c_1/c_2)$. For $b = a \in [1, m^*]$ we have

$$L(\boldsymbol{c}) = c_1^{a-1}\begin{pmatrix} y^{-a}{+}2a{-}1{+}a(a{-}1)\log y & -a\sqrt{y}(1{+}y^{-a}) \\ -a\sqrt{y}(1{+}y^{-a}) & y{+}y^{1-a}\big(2a{-}1{-}a(a{-}1)\log y\big) \end{pmatrix} \quad \text{with } y = c_1/c_2.$$

Because y and c_1 can be chosen independently, we have to show $L(\boldsymbol{c}) \geq 0$. Since the diagonal elements are non-negative it suffices to make the determinant non-negative as well. We have $\det L(\boldsymbol{c}) = c_1^{2a-2}\, y\, \ell_a(y)$ with

$$\ell_a(y) := \Big(\big(y^{-a}{+}2a{-}1 + (a^2{-}a)\log y\big)\big(1 + y^{-a}(2a{-}1{-}(a^2{-}a)\log y)\big) - a^2(1{+}y^{-a})^2\Big).$$

It is easily checked that $\ell_a(1) = \ell_a'(1) = 0$ and $\ell_a''(1) = 4a^2(a{-}1)(2{-}a)$. Thus, for $a = b > 2$ we have no lower bound for the eigenvalues of $L(\boldsymbol{c})$. For $a = b \in [1, 2]$ we summarize the positive result as follows.

Theorem 3.3 *For $a \in [1,2]$ the function*

$$(c_1, c_2) \mapsto (c_1^a - c_2^a)\log(c_1^a/c_2^a) \quad \textit{is convex.}$$

Consequently, for the two-species RDS (3.8) *with $b = a \in [1,2]$ the convexity method applies with $\mu = 0$, and we obtain the lower estimate*

$$K(\mathsf{q}) = \min\Big\{ \min\{\delta_1, \delta_2\}\rho_{\mathrm{lSo}}\,,\, 4\kappa\,\mathsf{q}^{a-1}\Big\}.$$

Proof. The first result follows from showing $\ell_a(y) \geq 0$. Setting $z = y^{-a}$ we need

$$\big(z + 2a - 1 - (a-1)\log z\big)\big(1 + z(2a-1+\log z\big) \geq a^2(1+z)^2 \quad \text{for all } z > 0,$$

but this can be checked easily by a numerical plot.

To obtain the lower bound for $K(\mathsf{q})$ we need to estimate the reactive decay rate k_{R} as defined in (2.14). Using $\mathsf{Q}\boldsymbol{c} = a(c_1+c_2) = \mathsf{q}$ and $\boldsymbol{w}(\mathsf{q}) = \frac{\mathsf{q}}{2a}(1,1)$, we set $\boldsymbol{c} = \frac{\mathsf{q}}{2a}(s, 2-s)$ with $s \in [0,2]$, then for $a \in [1,2]$ we have

$$\begin{aligned} k_{\mathrm{R}}(\mathsf{q}) &= \inf\Big\{ \frac{a(c_1^a - c_2^a)\log(c_1/c_2)}{H(\boldsymbol{c}|\boldsymbol{w}(\mathsf{q}))} \;\Big|\; \mathsf{Q}\boldsymbol{c} = \mathsf{q} \Big\} \\ &= \mathsf{q}^{a-1} \inf\Big\{ \frac{a(s^a - (2-s)^a)\log(s/(2-s))}{(2a)^{a-1}\big(\lambda_{\mathrm{B}}(s) + \lambda_{\mathrm{B}}(2-s)\big)} \;\Big|\; s \in [0,2] \Big\} \;\geq\; 4\mathsf{q}^{a-1}, \end{aligned}$$

where the last estimate follows by inspecting the graph of the function in the infimum numerically: the minimum is attained at $(s,a) \in \{(1,1),(1,2)\}$.

Now the lower estimate for $K(\mathsf{q})$ follows from Theorem 3.1 with $\mu = 0$. ∎

For the general case $1 \leq a < b$ we have

$$L(\boldsymbol{c}) = \Big(\frac{y^{(a-1)b}}{\rho^{b-1}}\Big)^{1/(b-a)} \begin{pmatrix} A_1(\rho) & -\sqrt{yA_2(\rho)} \\ -\sqrt{yA_2(\rho)} & yA_3(\rho) \end{pmatrix} \quad \text{with } \rho = c_1^a/c_2^b \text{ and } y = c_1/c_2.$$

The coefficient functions are given by

$$A_1(\rho) = 1 + \rho\big(2a-1+(a-1)\log\rho\big), \quad A_2(\rho) = ab(1+\rho)^2, \quad A_3(\rho) = \rho + 2b - 1 - (b-1)\log\rho.$$

In the case $a = 1$ it suffices to show that $L(\boldsymbol{c}) + \mu_1 \left(\begin{smallmatrix} 1 & 0 \\ 0 & 0 \end{smallmatrix}\right) \geq 0$ for some $\mu_1 \geq 0$, which is equivalent to

$$(A_1(\rho) + \rho\mu_1)A_3(\rho) \geq A_2(\rho) \iff \mu_1 \geq \widehat{\mu}(b) := \sup\Big\{ \frac{A_2(\rho) - A_1(\rho)A_3(\rho)}{\rho A_3(\rho)} \;\Big|\; \rho > 0 \Big\}.$$

Since the function in the supremum is continuous for $b \in \,]1, m^*[$ and converges to $b-1$ for $\rho \to \infty$ and to $-\infty$ for $\rho \to 0$, the supremum $M(b)$ exists for all $b \in [1, m^*[$. Of course, $\widehat{\mu}(1) = 0$ and $\widehat{\mu}(1) \approx 1.1675$, see Example 3.2. Numerically we find $(b-1)/(1 - b/m^*) \leq \widehat{\mu}(b) \leq 1.1(b-1)/(1 - b/m^*)$ for $b \in [1, m^*[$. We summarize this positive result as follows:

Theorem 3.4 *For $a = 1$ and $b \in [1, m^*[$ the convexity method is applicable to the two-species RDS* (3.8) *with the choice $\mu = \kappa\widehat{\mu}(b)$ giving the lower bound*

$$K(\mathsf{q}) \geq \min\Big\{ k_{\mathrm{R}}(\mathsf{q})\,,\, \delta_1\rho_{\mathrm{lSo}}\tfrac{k_{\mathrm{R}}(\mathsf{q})}{\kappa\widehat{\mu}(b) + k_{\mathrm{R}}(\mathsf{q})}\,,\, \delta_2\rho_{\mathrm{lSo}} \Big\}.$$

In the case $1 < a < b$, we can use that for fixed $\rho > 0$ the smaller eigenvalue of $\left(\begin{smallmatrix} A_1(\rho) & -(yA_2)^{1/2} \\ -(yA_2)^{1/2} & A_3(\rho) \end{smallmatrix}\right)$ converges to $n(\rho) := A_1(\rho) - A_2(\rho)/A_3(\rho)$ for $y \to \infty$. However, this value is still multiplied by y^c with a positive power $c = (a-1)b/(b-a)$. Hence, if there is a ρ with $n(\rho) < 0$, then the eigenvalues of $L(\boldsymbol{c})$ cannot be bounded from below. An explicit calculation gives $n(1) = 0$ and $n'(1) = 2(a-b)/b < 0$ such that $\rho > 1$ with $n(\rho) < 0$ always exists.

We conclude by stating our expectation that exploiting higher entropies (cf. [MHM15, Sec. 3.4]) allows us to widen the applicability of the convexity method for a much larger variety of cases.

3.4 The method of Desvillettes, Fellner, and Tang

In a series of papers starting with [DeF06, DeF07] and culminating with [DFT16] a more general method for the derivation of explicity energy-dissipation estimates was derived. We give a short overview of the Steps 1 to 4 in [FeT16, Sec. 2.2] to highlight the differences to the above convexity method. Of course, this general method avoids any convexity assumption of the type (3.5), which is rather restrictive, but gives simpler and sharper results if it is applicable. The general method uses several explicit estimates from functional analysis but needs to estimate some logarithmically growing terms from above.

For simplicity we restrict to the case with DBC (cf. (2.5)) and assume $\boldsymbol{c}_* = (1, .., 1)^\top$, but emphasize that RRE with the CBC can be handled as in [DFT16]. The major idea is to introduce the functions $a_i = \sqrt{c_i}$ and the vector $\boldsymbol{a} = (a_1, .., a_I)$ such that the two parts of the dissipation can be estimated via

$$\mathcal{D}_{\mathrm{D}}(\boldsymbol{c}) = \int_\Omega \sum_{i=1}^I \delta_i \Big(\frac{|\nabla c_i|^2}{2c_i} + 2|\nabla a_i|^2 \Big) \,\mathrm{d}x \ge \delta_{\min} \Big(\rho_{\mathrm{lSo}}(\Omega) \mathcal{H}(\boldsymbol{c}|\overline{\boldsymbol{c}}) + 2\|\nabla \boldsymbol{a}\|_{\mathrm{L}^2}^2 \Big) \text{ and}$$

$$\mathcal{D}_{\mathrm{R}}(\boldsymbol{c}) = \int_\Omega D_{\mathrm{R}}(\boldsymbol{c}(x)) \,\mathrm{d}x \ge \int_\Omega \sum_{n=1}^{R/2} 4\widehat{\kappa}_n \big| \boldsymbol{a}^{\boldsymbol{\alpha}^{S_n}} - \boldsymbol{a}^{\boldsymbol{\alpha}^{P_n}} \big|^2 \,\mathrm{d}x,$$

where we used the elementary inequality

$$\forall\, a, b > 0: \quad (a-b)\log(a/b) \ge 4\big(\sqrt{a} - \sqrt{b}\big)^2 \tag{3.9}$$

to estimate the reactive part from below. As above, for $\boldsymbol{c} \in \mathfrak{S}(\mathsf{q})$ we have $\mathcal{H}(\boldsymbol{c}|\overline{\boldsymbol{c}}) = \mathcal{H}(\boldsymbol{c}|\boldsymbol{w}_{\mathsf{q}}) + \mathcal{H}(\overline{\boldsymbol{c}}|\boldsymbol{w}_{\mathsf{q}})$, and we have to control the second term. For this, one introduces the continuous and increasing function

$$\Phi(z) = \frac{\lambda_{\mathrm{B}}(z)}{(\sqrt{z}-1)^2} = \log z + O(1)_{z\to\infty},$$

which provides the elementary estimate $\mathcal{H}(\overline{\boldsymbol{c}}|\boldsymbol{w}_{\mathsf{q}}) = H(\overline{\boldsymbol{c}}|\boldsymbol{w}_{\mathsf{q}}) =$

$$\sum_{i=1}^I H(\overline{c}_i|w_i^{\mathsf{q}}) = \sum_{i=1}^I \Phi(\overline{c}_i/w_i^{\mathsf{q}}) \big((\overline{c}_i)^{1/2} - (w_i^{\mathsf{q}})^{1/2} \big)^2 \ge \Phi(M) \sum_{i=1}^I \big((\overline{c}_i)^{1/2} - (w_i^{\mathsf{q}})^{1/2} \big)^2,$$

where the constant M is given by $\max\{\,\Phi(K_0/w_i^{\mathsf{q}}) \mid i=1,..,I\,\}$ with $K_0=\max\{\,\overline{c}_i \mid i=1,..,I\,\}$. Thus, one needs an upper bound for $\overline{c}_i$ which follows from $\lambda_{\mathrm{B}}(z)\geq z-2$ which gives $b\lambda_{\mathrm{B}}(a/b)\geq a-2b$ and hence

$$\mathcal{H}_{\mathsf{q}}(\boldsymbol{c})=\mathcal{H}(\boldsymbol{c}|\boldsymbol{w}_{\mathsf{q}})\geq\int_\Omega\sum_{i=1}^I\big(c_i(x)-2w_i^{\mathsf{q}}\big)\,\mathrm{d}x=\sum_{i=1}^I\overline{c}_i-W\text{ with }W=2\sum_{i=1}^I w_i^{\mathsf{q}}.$$

Since $\mathcal{H}_{\mathsf{q}}$ is a Liapunov function solutions satisfy

$$\overline{c_i(t)}\leq\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}(t))+W\leq\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}(0))+W=:K_0.$$

The most difficult part in this method is to find a constant $K_3(\mathsf{q})$ such that the estimate

$$\|\nabla\boldsymbol{a}\|_{\mathrm{L}^2}^2+\int_\Omega\sum_{n=1}^{R/2}\big(\boldsymbol{a}^{\boldsymbol{\alpha}^{S_n}}-\boldsymbol{a}^{\boldsymbol{\alpha}^{P_n}}\big)^2\,\mathrm{d}x\geq K_3\Big(\|\nabla\boldsymbol{a}\|_{\mathrm{L}^2}^2+\sum_{n=1}^{R/2}\Big(\overline{\boldsymbol{a}}^{\boldsymbol{\alpha}^{S_n}}-\overline{\boldsymbol{a}}^{\boldsymbol{\alpha}^{P_n}}\Big)^2\Big)\tag{3.10}$$

holds. The constant K_3 depends on the Poincare constant for Ω and polynomially on K_0 from above, where the degree of the polynomial depends on the maximum of $|\boldsymbol{\alpha}^r|$, since one exploits the Lipschitz continuity of $\boldsymbol{a}\mapsto\boldsymbol{a}^{\boldsymbol{\alpha}^r}$ on large balls.

In the final step it remains to show that the term $\|\nabla\boldsymbol{a}\|_{\mathrm{L}^2}^2$ can be used to control the mismatch between $\big((\overline{c}_i)^{1/2}\big)_i$ and $\overline{\boldsymbol{a}}$ such that the constraint $\mathsf{q}=\mathsf{Q}\overline{\boldsymbol{c}}$ can be exploited. We refer to [DFT16] for the full proof and conclude with some remarks of comparison.

Obviously, this method works in much more general cases than the convexity method. In both cases it is possible to derive explicit constants, however in the general method these constants are much more involved and cannot be interpreted as easily by the optimal decay rates of the diffusion alone and of the reactions alone.

Nevertheless, the central idea is quite similar: in both cases it is crucial to estimate suitable integral quantities by the corresponding averages, namely using Jensen's inequality in the convexity method (cf. the proof of Theorem 3.1) and (3.10) for the general method.

4 The Glitzky-Hünlich approach

In [GlH97] a general approach to derive global exponential decay rates was developed for electro-reaction-diffusion systems with reaction systems satisfying a detailed balance condition. The theory there is restricted to the two-dimensional case, but this restriction is only needed because of the coupling of the charges via the Poisson equation. We repeat the arguments and show how they simplify and generalize to arbitrary dimensions for uncharged particles.

Throughout we consider functions

$$\boldsymbol{c}\in\mathfrak{S}(\mathsf{q}):=\Big\{\,\boldsymbol{c}\in\mathrm{L}^1(\Omega)^I\;\Big|\;c_i\geq0,\quad\mathcal{Q}\boldsymbol{c}=\mathsf{Q}\overline{\boldsymbol{c}}=\mathsf{q}\,\Big\}.$$

We recall the energy-dissipation balance $\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}(t))=-\mathcal{D}(\boldsymbol{c}(t))$ with $\mathcal{H}_{\mathsf{q}}(\boldsymbol{c})=\mathcal{H}(\boldsymbol{c}|\boldsymbol{w}_{\mathsf{q}})=$

$\int_\Omega H(\boldsymbol{c}(x)|\boldsymbol{w}_\mathsf{q})\,\mathrm{d}x$, and the dissipation is estimated from below as follows:

$$\mathcal{D}(\boldsymbol{c}) \geq \delta\mathcal{D}_\mathrm{D}(\boldsymbol{c}) + \kappa\mathcal{D}_\mathrm{R}(\boldsymbol{c}) \quad \text{with } \delta,\kappa>0 \text{ where}$$
$$\mathcal{D}_\mathrm{D}(\boldsymbol{c}) = \int_\Omega \left(\sum_{i=1}^I \left|\nabla\sqrt{c_i}\right|^2\right)\mathrm{d}x \text{ and } \mathcal{D}_\mathrm{R}(\boldsymbol{c}) = \int_\Omega D_\mathrm{R}(\boldsymbol{c}(x))\,\mathrm{d}\,\mathrm{d}x.$$

Obviously, all $\boldsymbol{c}\in\mathfrak{S}(\mathsf{q})$ satisfy the equivalences

$$\mathcal{H}_\mathsf{q}(\boldsymbol{c})=0 \iff \boldsymbol{c}\equiv\boldsymbol{w}_\mathsf{q} \iff \mathcal{D}_\mathrm{D}(\boldsymbol{c})+\mathcal{D}_\mathrm{R}(\boldsymbol{c})=0 \iff \mathcal{D}(\boldsymbol{c})=0.$$

The following result is an adaptation of the results in [GlH97, Thm. 5.2], which rely on a non-constructive compactness argument. There the theory was developed for a semiconductor model involving a Poisson equation, which led to a restriction of the space dimension, namely $d\leq 2$. We will show that such a restriction is not necessary for pure RDS. We refer to [MiM16] for a generalization to the non-isothermal case. Note that this result is also somewhat weaker than the convexity method, since the decay constant $K(\mathsf{q},R)$ depends on R which is an upper bound for $\mathcal{H}_\mathsf{q}(\boldsymbol{c})$

Theorem 4.1 (General exponential decay) *Let $\Omega\subset\mathbb{R}^d$ with $d\in\mathbb{N}$ be a bounded domain with Lipschitz boundary. Furthermore assume that the unique-equilibrium condition* (2.13) *holds. Then,*

$$\forall\,\mathsf{q}\in\mathfrak{Q},\ R>0\ \exists\,K(\mathsf{q},R)>0\ \forall\,\boldsymbol{c}\in\mathfrak{S}(\mathsf{q})\ \textit{with}\ \mathcal{H}_\mathsf{q}(\boldsymbol{c})\leq R:\ \mathcal{D}(\boldsymbol{c})\geq K(\mathsf{q},R)\mathcal{H}_\mathsf{q}(\boldsymbol{c}). \tag{4.1}$$

Proof. Throughout this proof we fix $\mathsf{q}\in\mathfrak{Q}$ and write for simplicity $\boldsymbol{w}=\boldsymbol{w}_\mathsf{q}$.

In order to produce a contradiction, we assume that for all $n\in\mathbb{N}$ there exist $\boldsymbol{c}_{(n)}$ with

$$\mathcal{Q}(\boldsymbol{c}_{(n)})=\mathsf{q} \quad \text{and} \quad R\geq\mathcal{H}_\mathsf{q}(\boldsymbol{c}_{(n)})\geq n\mathcal{D}(\boldsymbol{c}_{(n)})\neq 0.$$

In particular, this implies $\mathcal{D}_\mathrm{D}(\boldsymbol{c}_{(n)})+\mathcal{D}_\mathrm{R}(\boldsymbol{c}_{(n)})\to 0$. Moreover, the bound $\mathcal{H}_\mathsf{q}(\boldsymbol{c}_{(n)})\leq R$ and the standard estimate $\lambda_\mathrm{B}(z)\geq(\sqrt{z}-1)^2$ provide the bounds

$$\left\|\nabla\sqrt{c_{(n)i}}\right\|_{\mathrm{L}^2}\to 0 \quad \text{and} \quad \left\|\sqrt{c_{(n)i}}\right\|_{\mathrm{L}^2}\leq C.$$

Thus, we conclude $\|\sqrt{c_{(n)i}}-\sqrt{a_i}\,\|_{\mathrm{H}^1}\to 0$ for a constant vector $\boldsymbol{a}=(a_1,..,a_I)$. By the strong convergence and the strong lower semicontinuity we have

$$\mathsf{Q}\boldsymbol{a}=\lim_{n\to\infty}\mathcal{Q}\boldsymbol{c}_{(n)}=\mathsf{q} \ \text{ and } \ 0\leq D_\mathrm{R}(\boldsymbol{a})=\mathcal{D}_\mathrm{R}(\boldsymbol{a})\leq\liminf_{n\to\infty}\mathcal{D}_\mathrm{R}(\boldsymbol{c}_{(n)})=0.$$

Hence, the UEC (2.13) implies $\boldsymbol{a}=\boldsymbol{w}$.

This in turn implies $\mathcal{H}_\mathsf{q}(\boldsymbol{c}_{(n)})\to 0$. To see this, we use that the convergence $\sqrt{c_{(n)i}}\to\sqrt{w_i}$ in H^1 implies the same convergence in L^{2p} for some $p>1$. Taking squares we find $c_{(n)i}\to w_i$ in L^p. Now the estimate $\lambda_\mathrm{B}(z)\leq C_p(1+z)^p$ and the continuity of λ_B imply the continuity of $\mathcal{H}_\mathsf{q}$ on $\mathrm{L}^p(\Omega)^I$ by Lebesgue's dominated convergence theorem. Hence, we conclude $\mathcal{H}_\mathsf{q}(\boldsymbol{c}_{(n)})\to\mathcal{H}_\mathsf{q}(\boldsymbol{w})=0$.

Continuing in our task to produce a contradiction we set

$$\lambda_n := \big(\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}_{(n)})\big)^{1/2} \to 0 \quad \text{and} \quad \boldsymbol{b}_{(n)} := \Psi(\lambda_n, \boldsymbol{c}_{(n)}),$$

where the mapping $\Psi(\lambda,\cdot)$ and its inverse $\Phi(\lambda,\cdot)$ are given by

$$\Psi(\lambda,\boldsymbol{c}) := \big(\frac{1}{\lambda}(c_i^{1/2}-w_i^{1/2})\big)_{i=1,..,I} \ \text{ and } \ \Phi(\lambda,\boldsymbol{b}) := \big((w_i^{1/2}+\lambda b_i)^2\big)_{i=1,..,I}.$$

For $\boldsymbol{b}_{(n)}$ we have the following two estimates

$$\|\nabla \boldsymbol{b}_{(n)}\|_{\mathrm{L}^2}^2 = \frac{1}{\lambda_N^2}\mathcal{D}_{\mathrm{D}}(\boldsymbol{c}_{(n)}) \le \frac{1}{n\lambda_n^2}\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}_{(n)}) = \frac{1}{n} \to 0.$$

$$\lambda_n^2 = \mathcal{H}_{\mathsf{q}}(\boldsymbol{c}_{(n)}) \ge \sum_{i=1}^{I} \Big\|\sqrt{c_{(n)i}}-\sqrt{w_i}\Big\|_{\mathrm{L}^2}^2 \ge \lambda_n^2 \big(\min_i w_i\big)\, \|\boldsymbol{b}_{(n)}\|_{\mathrm{L}^2}^2 \implies \|\boldsymbol{b}_{(n)}\|_{\mathrm{L}^2} \le C.$$

Thus, there exists a constant vector $\boldsymbol{d}$ such that $\boldsymbol{b}_{(n)} \to \boldsymbol{d}$ strongly in $\mathrm{H}^1(\Omega;\mathbb{R}^I)$.

To analyze the limit of the sequence $\frac{1}{\lambda_n^2}\mathcal{D}_{\mathrm{R}}(\boldsymbol{c}_{(n)})$ we use the function $\mathbb{D} : [0,1]\times\mathbb{R}^I \to [0,\infty]$ via

$$\mathbb{D}(\lambda,\boldsymbol{b}) = \begin{cases} \frac{1}{\lambda^2} D_{\mathrm{R}}(\Phi(\lambda,\boldsymbol{b})) & \text{for } \lambda > 0 \text{ and } (\lambda,\boldsymbol{b}) \in \mathrm{dom}(\mathbb{D}), \\ A(\boldsymbol{b}) & \text{for } \lambda = 0, \\ \infty & \text{otherwise,} \end{cases}$$

$$\text{where } \mathrm{dom}(\mathbb{D}) = \{\, (\lambda,\boldsymbol{b}) \in [0,1]\times\mathbb{R}^I \mid \forall\, i:\ w_i^{1/2}+\lambda b_i \ge 0 \,\}$$

$$\text{and } A(\boldsymbol{b}) = 2\boldsymbol{b}\cdot\mathbb{W}^{1/2}\mathbb{H}\mathbb{W}^{1/2}\boldsymbol{b}.$$

Here $\mathbb{W} = \mathrm{diag}(w_1,..,w_I)$ and $\mathbb{H} \ge 0$ is the Hessian $\mathrm{D}^2 D_{\mathrm{R}}(\boldsymbol{w})$. By construction the function $\mathbb{D}$ is lower semi-continuous, since A is simply the limit of $\mathbb{D}(\lambda,\cdot) = D_{\mathrm{R}}(\Phi(\lambda,\cdot)/\lambda^2$, where we use the expansion $\Phi(\lambda,\boldsymbol{b}) = \boldsymbol{w} + 2\lambda\mathbb{W}^{1/2}\boldsymbol{b} + O(|\lambda\boldsymbol{b}|^2)$.

Using $\boldsymbol{b}_{(n)} \to \boldsymbol{d}$ in $\mathrm{H}^1(\Omega)$ provides a subsequence such that $\boldsymbol{b}_{(n)}(x) \to \boldsymbol{d}$ a.e. in Ω. Since by construction we have $\int_\Omega \mathbb{D}(\lambda_n,\boldsymbol{b}_{(n)})\,\mathrm{d}x = \mathcal{D}_{\mathrm{R}}(\boldsymbol{c}_{(n)})/\lambda_n^2$, the lower semicontinuity and positivity of $\mathbb{D}$ and Fatou's lemma yield

$$\begin{aligned} A(\boldsymbol{d}) &= \int_\Omega \mathbb{D}(0,\boldsymbol{d})\,\mathrm{d}x \le \liminf_{k\to\infty} \int_\Omega \mathbb{D}(\lambda_{n_k},\boldsymbol{b}_{(n_k)})\,\mathrm{d}x \\ &= \lim_{k\to\infty} \frac{1}{\lambda_{n_k}^2}\mathcal{D}_{\mathrm{R}}(\boldsymbol{c}_{(n)}) = \lim_{k\to\infty} \frac{1}{n_k\lambda_{n_k}^2}\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}_{(n)}) = 0. \end{aligned}$$

The UEC (2.13) and the CBC for the mass-action structure imply that the Hessian $\mathbb{H} = \mathrm{D}^2 D_{\mathrm{R}}(\boldsymbol{w})$ has a well-defined kernel, namely exactly the one given by the linearization at $\boldsymbol{w}$ of set of all equilibria $\boldsymbol{w}_{\widetilde{\mathsf{q}}}$ for $\widetilde{\mathsf{q}} \in \mathfrak{Q}$. Thus, the explicit formula (2.12) shows $\mathrm{kernel}(\mathbb{K}) = \mathbb{W}\mathbb{S}^\perp$, such that $A(\boldsymbol{d}) = 0$ implies $\mathbb{W}^{-1/2}\boldsymbol{d} \in \mathbb{S}^\perp$.

Moreover, $\mathsf{q} = \mathsf{Q}\boldsymbol{w} = \mathcal{Q}(\boldsymbol{c}_{(n)})$ and the strong L^2 convergence $\boldsymbol{b}_{(n)} \to \boldsymbol{d}$ imply

$$0 = \frac{1}{\lambda_n}\Big(\mathcal{Q}\big(\Phi(\lambda_n,\boldsymbol{b}_{(n)})\big) - \mathsf{Q}\boldsymbol{w}\Big) \ \to \ 2\mathsf{Q}\mathbb{W}^{1/2}\boldsymbol{d}.$$

This implies $\mathbb{W}^{1/2}\boldsymbol{d} \in \mathbb{S}$. Since we already know $\mathbb{W}^{-1/2}\boldsymbol{d} \in \mathbb{S}^{\perp}$, we arrive at

$$0 = \mathbb{W}^{-1/2}\boldsymbol{d} \cdot \mathbb{W}^{1/2}\boldsymbol{d} = |\boldsymbol{d}|^2. \tag{4.2}$$

To generate the desired contradiction we introduce the function

$$\widetilde{H}(\lambda, b) = \begin{cases} \frac{1}{\lambda^2}\lambda_{\mathrm{B}}((1+\lambda b)^2) & \text{for } 1+\lambda b \geq 0 \text{ and } \lambda > 0, \\ 2b^2 & \text{for } \lambda = 0, \\ \infty & \text{otherwise.} \end{cases}$$

Note that $\widetilde{H}$ is continuous on its domain $\mathrm{dom}(\widetilde{H}) = \{\, (\lambda, b) \in [0,1]\times\mathbb{R} \,|\, 1+\lambda b \geq 0 \,\}$, which is closed. Moreover, using $(\sqrt{z}-1)^2 \leq \lambda_{\mathrm{B}}(z) \leq C_p(\sqrt{z}-1)^2(1+z)^p$ we have $b^2 \leq \widetilde{H}(\lambda, b) \leq b^2 C_p(3+2\lambda^2 b^2)^p$ on the domain. Thus,

$$\begin{aligned} 1 &= \frac{1}{\lambda_n^2}\mathcal{H}_{\mathsf{q}}(\boldsymbol{c}_{(n)}) = \frac{1}{\lambda_n^2}\mathcal{H}_{\mathsf{q}}\big(\Phi(\lambda_n, \boldsymbol{b}_{(n)})\big) \\ &= \int_\Omega \Big(\sum_{i=1}^I w_i \widetilde{H}\big(\lambda_n, b_{(n)i}/w_i^{1/2}\big)\Big)\,\mathrm{d}x \quad \overset{n\to\infty}{\to} \quad \int_\Omega \Big(\sum_{i=1}^I 2d_i^2 \Big)\,\mathrm{d}x \;=\; 2|\boldsymbol{d}|^2, \end{aligned} \tag{4.3}$$

where we used $\boldsymbol{b}_n \to \boldsymbol{d}$ in $\mathrm{H}^1(\Omega)^I$ and that the functional defined via $\widetilde{H}$ is continuous on $\mathrm{H}^1(\Omega)^I \subset \mathrm{L}^{2p}(\Omega)^I$ because of the continuity of and the upper bound for $\widetilde{H}$.

Thus, (4.2) and (4.3) provide the desired contradiction, and proof is finished. ∎

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