

EDP-convergence for nonlinear fast-slow reaction systems with detailed balance

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Abstract

We consider nonlinear reaction systems satisfying mass-action kinetics with slow and fast reactions. It is known that the fast-reaction-rate limit can be described by an ODE with Lagrange multipliers and a set of nonlinear constraints that ask the fast reactions to be in equilibrium. Our aim is to study the limiting gradient structure which is available if the reaction system satisfies the detailed-balance condition.

The gradient structure on the set of concentration vectors is given in terms of the relative Boltzmann entropy and a cosh-type dissipation potential. We show that a limiting or effective gradient structure can be rigorously derived via EDP convergence, i.e. convergence in the sense of the Energy-Dissipation Principle for gradient flows. In general, the effective entropy will no longer be of Boltzmann type and the reactions will no longer satisfy mass-action kinetics.

1 Introduction

The study of nonlinear reaction systems with different time scales has attracted much attention over the last decades, see e.g. [Bot03, KaK13, WiS17, DLZ18, MiS19, MaM20] and the references therein. In this work we consider the simplest case of fast-slow reaction systems with mass-action kinetics that have only two time scales, namely 1 and ε ,

$$\dot{c} = \mathbf{R}_{\text{sl}}(c) + \frac{1}{\varepsilon} \mathbf{R}_{\text{fa}}(c), \quad (1.1)$$

where $c \in \mathbf{C} := [0, \infty[^{i^*}$ denotes the vector of the concentrations c_i of the i^{th} species X_i . The typical aim of the above-mentioned work is to derive the limiting equation for the evolution of c on the slow time scale, while the fast reactions are in equilibrium. Under suitable assumptions the limiting equation can be formulated in three equivalent ways:

$$\text{constrained dynamics: } \dot{c}(t) = \mathbf{R}_{\text{sl}}(c(t)) + \lambda(t), \quad \lambda(t) \in \Gamma_{\text{fa}} \subset \mathbb{R}^{i^*}, \quad \mathbf{R}_{\text{fa}}(c(t)) = 0,$$

$$\text{projected dynamics: } \dot{c}(t) = (I - \mathbb{P}(c(t))) \mathbf{R}_{\text{sl}}(c(t)), \quad \mathbf{R}_{\text{fa}}(c(0)) = 0,$$

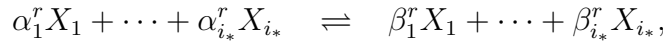
$$\text{reduced dynamics: } \dot{q}(t) = Q_{\text{fa}} \mathbf{R}_{\text{sl}}(\Psi(q(t))), \quad c(t) = \Psi(q(t)).$$

We refer to Section 4 for a discussion of these formulations.

The goal of this work is to revisit the same limit process, but now from the point of view of variational evolution. Our starting point is that reaction-rate equations such as (1.1) can be written as a gradient-flow equation if the reactions occur in pairs of forward and backward reactions and that these pairs satisfy the *detailed-balance condition*. This observation was highlighted in [Mie11, Sec. 3.1] but was observed and used implicitly earlier in [ÖtG97, Eqs. (103)+(113)] and [Yon08, Sec. VII]. A different

gradient structure already occurs in [Grm10, Eqn. (69)] and has its origin in the thermodynamic considerations in [Mar15] from 1915. The latter gradient structure, which we will call the *cosh-type gradient structure* following [MiS19], was mathematically derived in [MPR14, MP*17] from microscopic chemical master equations via a large-deviation principle.

To be specific, we assume that the species X_i , $i \in I := \{1, \dots, i_*\}$ undergo r_* forward-backward reactions of mass-action type



where $\alpha^r = (\alpha_i^r)_{i \in I}$ and $\beta^r = (\beta_i^r)_{i \in I}$ are the stoichiometric vectors in $\mathbb{N}_0^{i_*}$. The reaction-rate equation (1.1) takes the form

$$\dot{c} = - \sum_{r=1}^{r_*} (k_r^{\text{fw}} c^{\alpha^r} - k_r^{\text{bw}} c^{\beta^r}) (\alpha^r - \beta^r), \quad \text{where } c^\alpha = c_1^{\alpha_1} \dots c_{i_*}^{\alpha_{i_*}}. \quad (1.2)$$

The *detailed-balance condition* asks for the existence of a positive concentration vector $c_* = (c_i^*)_{i \in I} \in \mathbf{C}_+ :=]0, \infty[^{i_*}$ such that all r_* reactions are in

$$\exists c_* = (c_i^*)_{i \in I} \in \mathbf{C}_+ \forall r \in R := \{1, \dots, r_*\} : k_r^{\text{fw}} c_*^{\alpha^r} = k_r^{\text{bw}} c_*^{\beta^r}. \quad (1.3)$$

For the subsequent analysis it is advantageous to introduce the scalars $\delta_r^* = (c_*^{\alpha^r} c_*^{\beta^r})^{1/2}$ and $\widehat{\kappa}_r = k_r^{\text{fw}} c_*^{\alpha^r} / \delta_r^* = k_r^{\text{bw}} c_*^{\beta^r} / \delta_r^*$.

Throughout this work we will assume that c_* will not depend on the small parameter ε measuring the ratio between the slow and the fast time scale. The set of reaction pairs R will be decomposed into slow and fast reactions, namely $R = R_{\text{sl}} \dot{\cup} R_{\text{fa}}$, and we assume $\widehat{\kappa}_r = \kappa_r$ for $r \in R_{\text{sl}}$ and $\widehat{\kappa}_r = \kappa_r / \varepsilon$ for $r \in R_{\text{fa}}$, where κ_r are fixed numbers. With this we obtain the symmetric representation of the fast-slow reaction-rate equation via

$$\dot{c} = \mathbf{R}_{\text{sl}}(c) + \frac{1}{\varepsilon} \mathbf{R}_{\text{fa}}(c) \quad \text{with } \mathbf{R}_{\text{xy}}(c) := - \sum_{r \in R_{\text{xy}}} \kappa_r \delta_r^* \left(\frac{c^{\alpha^r}}{c_*^{\alpha^r}} - \frac{c^{\beta^r}}{c_*^{\beta^r}} \right) (\alpha^r - \beta^r). \quad (1.4)$$

The cosh-type gradient structure is now defined in terms of a gradient system $(\mathbf{C}, \mathcal{E}, \mathcal{R}_\varepsilon^*)$, where the energy functional is given in terms of the relative Boltzmann entropy

$$\mathcal{E}(c) = \sum_{i \in I} c_i^* \lambda_B(c_i / c_i^*), \quad \text{where } \lambda_B(\rho) := \rho \log \rho - \rho + 1,$$

and the dual dissipation potential $\mathcal{R}_\varepsilon^*$ in the form

$$\mathcal{R}_\varepsilon^*(c, \xi) = \mathcal{R}_{\text{sl}}^*(c, \xi) + \frac{1}{\varepsilon} \mathcal{R}_{\text{fa}}^*(c, \xi) \quad \text{with } \mathcal{R}_{\text{xy}}^*(c, \xi) = \sum_{r \in R_{\text{xy}}} \kappa_r (c^{\alpha^r} c^{\beta^r})^{1/2} C^*((\alpha^r - \beta^r) \cdot \xi),$$

where $C^*(\zeta) = 4 \cosh(\zeta/2) - 4$. The fast-slow reaction-rate equation (1.4) can now be written as the gradient flow equation

$$\dot{c}(t) = \partial_\xi \mathcal{R}_\varepsilon^*(c(t), -D\mathcal{E}(c(t))).$$

In fact, there are many other gradient structures for (1.4), see Remark 2.6; however the cosh-type gradient structure is special in several aspects: (i) it can be derived via large-deviation principles [MPR14, MP*17], (ii) the dual dissipation potential \mathcal{R}^* is independent of c_* , and (iii) it is stable under

general limiting processes, see [LM*17, Sec. 3.3]. The property (ii), also called *tilt invariance* below, will be especially important for us.

The main goal of this paper is to construct the effective gradient system $(\mathbf{C}, \mathcal{E}_{\text{eff}}, \mathcal{R}_{\text{eff}}^*)$ for the given family $(\mathbf{C}, \mathcal{E}, \mathcal{R}_\varepsilon^*)$ in the limit $\varepsilon \rightarrow 0^+$. Here we use the notion of *convergence of gradient system in the sense of the energy-dissipation principle*, shortly called *EDP-convergence*. This convergence notion was introduced in [DFM19] and further developed in [MMP19, FrL19, MiS19] and is based on the dissipation functionals

$$\mathfrak{D}_\varepsilon^\eta(c) := \int_0^T \{ \mathcal{R}_\varepsilon(c, \dot{c}) + \mathcal{R}_\varepsilon^*(c, \eta - D\mathcal{E}(c)) \} dt,$$

which are defined for all curves $c \in L^1([0, T]; \mathbf{C})$. The notion of *EDP-convergence with tilting* now asks that the two Γ -convergences $\mathcal{E}_\varepsilon \xrightarrow{\Gamma} \mathcal{E}_{\text{eff}}$ and $\mathfrak{D}_\varepsilon^\eta \xrightarrow{\Gamma} \mathfrak{D}_0^\eta$ (in suitable topologies) and that for all η the limit \mathfrak{D}_0^η has the form $\mathfrak{D}_0^\eta(c) = \int_0^T \{ \mathcal{R}_{\text{eff}}(c, \dot{c}) + \mathcal{R}_{\text{eff}}^*(c, \eta - D\mathcal{E}(c)) \} dt$; see Section 3.1 for the exact definition.

Our main result is Theorem 3.5 which asserts EDP-convergence with tilting with

$$\mathcal{E}_{\text{eff}} = \mathcal{E} \quad \text{and} \quad \mathcal{R}_{\text{eff}}^*(c, \xi) = \mathcal{R}_{\text{sl}}^*(c, \xi) + \chi_{\Gamma_{\text{fa}}^\perp}(\xi),$$

where $\Gamma_{\text{fa}} = \text{span} \{ \alpha^r - \beta^r \mid r \in R_{\text{fa}} \}$, $\Gamma_{\text{fa}}^\perp := \{ \xi \in \mathbb{R}^{i_*} \mid \forall \gamma \in \Gamma_{\text{fa}} : \gamma \cdot \xi = 0 \}$ and χ_A is the characteristic function of convex analysis taking 0 on A and ∞ otherwise. The proof relies on three observations:

(1) Tilting of the relative Boltzmann entropy \mathcal{E} by η is equivalent to changing the underlying equilibrium c_* to $c_*^\eta := (e^{\eta_i} c_i^*)_{i \in I}$ (see (3.7)), and $\mathcal{R}_\varepsilon^*$ is independent of c_*^η .

(2) The dual dissipation potentials $\mathcal{R}_\varepsilon^*$ increase monotonically to their limit $\mathcal{R}_{\text{eff}}^*$, which is singular. Hence, the primal dissipation potentials \mathcal{R}_ε decrease monotonically to their limit \mathcal{R}_{eff} , which is degenerate. Defining $Q_{\text{fa}} : \mathbb{R}^{i_*} \rightarrow \mathbb{R}^{m_{\text{fa}}}$ such that $\ker Q_{\text{fa}} = \Gamma_{\text{fa}}$ and $\text{im } Q_{\text{fa}}^\top = \Gamma_{\text{fa}}^\perp$, the bound $\mathfrak{D}_\varepsilon^\eta(c^\varepsilon) \leq M_{\text{diss}} < \infty$ does not provide a uniform bound on \dot{c}^ε , but we are able to show weak compactness of $Q_{\text{fa}} \dot{c}^\varepsilon$ in $W^{1,1}([0, T]; \mathbb{R}^{m_{\text{fa}}})$.

(3) To obtain compactness for families $(c^\varepsilon)_{\varepsilon \in]0,1[}$ from the bound $\mathfrak{D}_\varepsilon(c^\varepsilon) \leq M_{\text{diss}} < \infty$ we can use $\int_0^T \mathcal{R}_{\text{fa}}^*(c^\varepsilon, -D\mathcal{E}(c^\varepsilon)) dt \leq \varepsilon M_{\text{diss}}$, which forces c^ε into the set of equilibria of the fast equation, namely $\mathcal{E}_{\text{fa}} := \{ c \in \mathbf{C} \mid \mathbf{R}_{\text{fa}}(c) = 0 \}$.

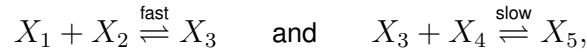
An important assumption of the fast reaction system $c'(\tau) = \mathbf{R}_{\text{fa}}(c(\tau))$ is that it has a unique equilibrium in each invariant subset $\mathbf{C}_{\mathbf{q}}^{\text{fa}} := \{ c \in \mathbf{C} \mid Q_{\text{fa}} c = \mathbf{q} \}$. This equilibrium is obtained as minimizer of \mathcal{E} and is denoted by $\Psi(\mathbf{q})$. Thus, the *unique fast equilibrium condition* reads

$$\mathcal{M}_{\text{sl}} := \{ \Psi(\mathbf{q}) \mid \mathbf{q} \in Q_{\text{fa}} \mathbf{C} \} \stackrel{!!}{=} \mathcal{E}_{\text{fa}} := \{ c \in \mathbf{C} \mid \mathbf{R}_{\text{fa}}(c) = 0 \}.$$

The main difficulty is to show that the information in points (2) and (3) is enough to obtain the compactness necessary for deriving liminf estimate for the Γ -convergence $\mathfrak{D}_\varepsilon \xrightarrow{\Gamma} \mathfrak{D}_0$ for the non-convex functionals \mathfrak{D}_ε . On the local level, one sees that (2) provides partial control of the temporal oscillations of \dot{c}^ε via the bound on $Q_{\text{fa}} \dot{c}^\varepsilon$ in $L^1([0, T]; \mathbb{R}^{m_{\text{fa}}})$, whereas (3) provides strong convergence towards \mathcal{M}_{sl} , which is locally defined via $D\mathcal{E}(c) \in \Gamma_{\text{fa}}^\perp$ (see Lemma 3.7). In summary, we are able to show that $\mathfrak{D}_\varepsilon(c^\varepsilon) \leq M_{\text{diss}} < \infty$ implies that there exists a subsequence such that $c^{\varepsilon_n} \rightarrow \tilde{c}$ in $L^1([0, T]; \mathbf{C})$ and $Q_{\text{fa}} \dot{c}^{\varepsilon_n} \rightarrow \mathbf{q}$ uniformly in $C^0([0, T]; \mathbb{R}^{m_{\text{fa}}})$, where $\tilde{c}(t) = \Psi(\mathbf{q}(t))$ with $\mathbf{q} \in W^{1,1}([0, T]; \mathbb{R}^{m_{\text{fa}}})$.

As a corollary we obtain that the limiting evolution lies in \mathcal{M}_{sl} and is governed by the reduced (or coarse grained) equation $\dot{\mathbf{q}} = Q_{\text{fa}} \mathbf{R}_{\text{sl}}(\Psi(\mathbf{q}))$ described by the slow variables $\mathbf{q} \in Q_{\text{fa}} \mathbf{C}$ and a natural gradient structure $(Q_{\text{fa}} \mathbf{C}, E, R)$. Even on the level of the limiting equations our result goes beyond those in [Bot03, DLZ18], since we do not assume that solutions are strictly positive or that the stoichiometric vectors $\gamma^r = \alpha^r - \beta^r$, $r \in R_{\text{fa}}$, are linearly independent.

For illustration, we close the introduction by a simple example involving $i_* = 5$ species and one fast and one slow reaction (see Section 4.3 for the details under slightly more general conditions):



which gives rise to the stoichiometric vectors $\gamma^{\text{fa}} = (1, 1, -1, 0, 0)^\top$ and $\gamma^{\text{sl}} = (0, 0, 1, 1, -1)^\top$. Assuming the detailed-balance condition with respect to the steady state $c_* = (1, 1, 1, 1, 1)^\top$, the reaction-rate equation takes the form

$$\dot{c} = -\frac{\kappa^{\text{fa}}}{\varepsilon} (c_1 c_2 - c_3) \gamma^{\text{fa}} - \kappa^{\text{sl}} (c_3 c_4 - c_5) \gamma^{\text{sl}}.$$

The limiting reaction system can be described by the slow variables $\mathbf{q} = (c_1 + c_3, c_2 + c_3, c_4, c_5)^\top$ and reads

$$\dot{\mathbf{q}} = Q_{\text{fa}} \mathbf{R}_{\text{sl}}(\Psi(\mathbf{q})) = -\kappa^{\text{sl}} (a(q_1, q_2) q_3 - q_4) \gamma^{\text{sl}},$$

where the slow manifold takes the form $\Psi(\mathbf{q}) = (q_1, q_2, a(q_1, q_2), q_3, q_4)$ and the reduced entropy is $E(\mathbf{q}) = \mathcal{E}(\Psi(\mathbf{q}))$.

2 Modeling of reaction systems

We first introduce the classical notation for reaction systems with reaction kinetics according to the mass-action law. After briefly recalling our notation for *gradient systems*, we show that based on the condition of detailed balance, the reaction-rate equation is the gradient-flow equation for a suitable gradient system. Next we introduce our class of fast-slow systems, and finally we present a small, but nontrivial example in \mathbb{R}^3 .

2.1 Mass action law and stoichiometric subspaces

We consider $i_* \in \mathbb{N}$ species X_i reacting with each other by $r_* \in \mathbb{N}$ reactions. The set of species is denoted by $I = \{1, \dots, i_*\}$, the set of reactions by $R = \{1, \dots, r_*\}$, and the r_* chemical reactions are given by

$$\forall r \in R : \sum_{i=1}^{i_*} \alpha_i^r X_i \rightleftharpoons \sum_{i=1}^{i_*} \beta_i^r X_i,$$

where the stoichiometric vectors $\alpha^r, \beta^r \in \mathbb{N}_0^{i_*}$ contain the stoichiometric coefficients. The concentration c_i of species X_i is nonnegative, the space of concentrations is denoted by

$$\mathbf{C} = [0, \infty[^{i_*} \subset \mathbb{R}^{i_*},$$

which is the nonnegative cone of \mathbb{R}^{i_*} . Moreover, we introduce $\mathbf{C}_+ := \text{int } \mathbf{C} =]0, \infty[^{i_*}$, the interior of the set of concentrations.

The mass-action law for reaction kinetics assumes that the forward and backward reaction fluxes are proportional to the product of the densities of the species, i.e. $j(c)_r = -k_r^{\text{fw}} c^{\alpha^r} + k_r^{\text{bw}} c^{\beta^r}$, where for stoichiometric vectors $\delta \in \mathbb{N}_0^{i^*}$ the monomials c^δ are given by $\prod_{i=1}^{i^*} c_i^{\delta_i}$. The reaction-rate equation (RRE) of the concentrations $c \in \mathbf{C}$ takes the form

$$\dot{c} = \mathbf{R}(c) = - \sum_{r=1}^{r_*} (k_r^{\text{fw}} c^{\alpha^r} - k_r^{\text{bw}} c^{\beta^r}) (\alpha^r - \beta^r), \quad (2.1)$$

with given forward and backward reaction rates $k_r^{\text{fw}}, k_r^{\text{bw}} > 0$.

For each of the r reactions we introduce the stoichiometric vector $\gamma^r := \alpha^r - \beta^r \in \mathbb{Z}^{i^*}$. The span of all vectors γ^r is the *stoichiometric subspace* $\Gamma \subset \mathbb{R}^{i^*}$, i.e. $\Gamma := \text{span} \{ \gamma^r \mid r \in R \}$. We do not assume any properties of the stoichiometric vectors, in particular they are not assumed to be linearly independent.

Conservation directions are vectors $q \in \mathbb{R}^{i^*}$ such that $q \in \Gamma^\perp$ (also written $q \perp \Gamma$), where the annihilator Γ^\perp is defined as $\Gamma^\perp = \{ q \in \mathbb{R}^{i^*} \mid \forall \gamma \in \Gamma : q \cdot \gamma = 0 \}$. By construction we have $\mathbf{R}(c) \in \Gamma$, thus for all solutions $t \mapsto c(t)$ of the RRE (2.1), the value of $q \cdot c(t)$ is constant, i.e. $q \cdot c$ is a conserved quantity for (2.1). Fixing a basis $\{q_1, \dots, q_m\}$ of Γ^\perp , we introduce a matrix $Q \in \mathbb{R}^{m \times i^*}$ by defining its adjoint $Q^\top = (q_1, \dots, q_m)$. By construction, $Q^\top : \mathbb{R}^m \rightarrow \mathbb{R}^{i^*}$ is injective, $Q : \mathbb{R}^{i^*} \rightarrow \mathbb{R}^m$ is surjective, and $\ker Q = \Gamma$. The image of the nonnegative cone \mathbf{C} under Q is denoted by \mathcal{Q} , i.e. $Q : \mathbf{C} \rightarrow \mathcal{Q} \subset \mathbb{R}^m$. Fixing a vector $q \in \mathcal{Q}$, we define the stoichiometric subsets

$$\mathbf{C}_q := \{ c \in \mathbf{C} \mid Qc = q \}.$$

They provide a decomposition $\mathbf{C} = \cup_{q \in \mathcal{Q}} \mathbf{C}_q$ into affine sets that are invariant under the flow of the RRE (2.1).

Notation: In the whole paper we consider all vectors as column vectors. In particular $D\mathcal{E}(c) \in X^*$ is also a column vector although it is an element of the dual space and might be understood as a covector.

2.2 Notations for gradient systems

Following [Mie11, Mie16], we call a triple $(\mathbf{X}, \mathcal{E}, \mathcal{R})$ a (generalized) *gradient system* (GS) if

- 1) the state space \mathbf{X} is a closed and convex subspace of a Banach space X ,
- 2) $\mathcal{E} : \mathbf{X} \rightarrow \mathbb{R}_\infty := \mathbb{R} \cup \{\infty\}$ is a sufficiently smooth functional (such as a free energy, a relative entropy, or a negative entropy, etc.),
- 3) $\mathcal{R} : \mathbf{X} \times X \rightarrow \mathbb{R}_\infty$ is a dissipation potential, which means that for any $u \in \mathbf{X}$ the functional $\mathcal{R}(u, \cdot) : X \rightarrow \mathbb{R}_\infty$ is lower semicontinuous, nonnegative and convex, and satisfies $\mathcal{R}(u, 0) = 0$.

The dynamics of a gradient system is given by the associated *gradient-flow equation* that can be formulated in three different, but equivalent ways: as an equation in X , in \mathbb{R} , or in X^* (the dual Banach space of X), respectively:

$$(I) \text{ Force balance in } X^* : \quad 0 \in \partial_{\dot{u}} \mathcal{R}(u, \dot{u}) + D\mathcal{E}(u) \in X^*, \quad (2.2a)$$

$$(II) \text{ Power balance in } \mathbb{R} : \quad \mathcal{R}(u, \dot{u}) + \mathcal{R}^*(u, -D\mathcal{E}(u)) = -\langle D\mathcal{E}(u), \dot{u} \rangle \in \mathbb{R}, \quad (2.2b)$$

$$(III) \text{ Rate equation in } X : \quad \dot{u} \in \partial_{\xi} \mathcal{R}^*(u, -D\mathcal{E}(u)) \subset X. \quad (2.2c)$$

Here, \mathcal{R}^* is the *dual dissipation potential* obtained by Legendre-Fenchel transform, $\mathcal{R}^*(u, \xi) := \sup_{v \in X} \{\langle \xi, v \rangle - \mathcal{R}(u, v)\}$. The partial derivatives $\partial_{\dot{u}} \mathcal{R}(u, \dot{u})$ and $\partial_{\xi} \mathcal{R}^*(u, \xi)$ are the possibly set-valued convex subdifferentials.

For a given evolution equation $\dot{u} = \mathbf{V}(u)$ we say that it has a *gradient structure* if there exists a gradient system $(\mathbf{X}, \mathcal{E}, \mathcal{R})$ such that the evolution equation is the gradient-flow equation for this gradient system, namely $\mathbf{V}(u) = \partial_{\xi} \mathcal{R}^*(u, -D\mathcal{E}(u))$. We emphasize that a given evolution equation may have none or many gradient structures; see Remark 2.6 for the case of our nonlinear reaction systems.

Integrating the power balance (II) in time over $[0, T]$ and using the chain rule for the time-derivative of $t \mapsto \mathcal{E}(u(t))$, we obtain another equivalent formulation of the dynamics of the gradient system, which is called *Energy-Dissipation-Balance*:

$$(EDB) \quad \mathcal{E}(u(T)) + \int_0^T \{\mathcal{R}(u, \dot{u}) + \mathcal{R}^*(u, -D\mathcal{E}(u))\} dt = \mathcal{E}(u(0)). \quad (2.3)$$

This gives rise to the *dissipation functional*

$$\mathfrak{D}(u) := \int_0^T \{\mathcal{R}(u, \dot{u}) + \mathcal{R}^*(u, -D\mathcal{E}(u))\} dt,$$

which is now defined on trajectories $u : [0, T] \mapsto \mathbf{X}$.

The following *Energy-Dissipation Principle* (EDP) states that, under natural technical conditions, solving the EDB (2.3) is equivalent to solving any of the three versions of the gradient-flow equation (2.2).

Theorem 2.1 (Energy-dissipation principle, cf. [AGS05, Prop. 1.4.1] or [Mie16, Th. 3.2]). *Assume that \mathbf{X} is a closed convex subset of $X = \mathbb{R}^{i_*}$, that $\mathcal{E} \in C^1(\mathbf{X}, \mathbb{R})$, and that the dissipation potential $\mathcal{R}(u, \cdot)$ is superlinear uniformly in $u \in \mathbf{X}$. Then, a function $u \in W^{1,1}([0, T]; \mathbb{R}^{i_*})$ is a solution of the gradient-flow equation (2.2) if and only if u solves the EDB (2.3).*

2.3 The detailed balance condition induces gradient structures

Already in Section 2.1, we have assumed that each reaction occurs in both forward and backward directions. Such reaction systems are called *weakly reversible*. A much stronger assumption is the so-called *detailed-balance condition* which states that there is a strictly positive state $c_* = (c_i^*) \in \mathbf{C}_+$ in which all reactions are in equilibrium, i.e. $j_r(c_*) = 0$ for all r :

$$(DBC) \quad \exists c_* \in \mathbf{C}_+ \forall r \in \mathbb{R} : k_r^{\text{fw}} c_*^{\alpha^r} = k_r^{\text{bw}} c_*^{\beta^r}. \quad (2.4)$$

Under this assumption, one can rewrite the RRE (2.1) in the symmetric form

$$\dot{c} = \mathbf{R}(c) = - \sum_{r=1}^{r_*} \widehat{\kappa}_r \delta_r^* \left(\frac{c^{\alpha^r}}{c_*^{\alpha^r}} - \frac{c^{\beta^r}}{c_*^{\beta^r}} \right) (\alpha^r - \beta^r) \quad (2.5)$$

with $\delta_r^* = (c_*^{\alpha^r} c_*^{\beta^r})^{1/2}$ and $\widehat{\kappa}_r := k_r^{\text{fw}} c_*^{\alpha^r} / \delta_r^* = k_r^{\text{bw}} c_*^{\beta^r} / \delta_r^*$.

Subsequently, we will use the notion of a *reaction system satisfying the detailed-balance condition*, or shortly a detailed-balance reaction system.

Definition 2.2 (Detailed-balance reaction systems (DBRS)). For $i_*, r_* \in \mathbb{N}$ consider the stoichiometric matrices $A = (\alpha_i^r) \in \mathbb{N}_0^{i_* \times r_*}$ and $B = (\beta_i^r) \in \mathbb{N}_0^{i_* \times r_*}$ and the vectors $c_* = (c_i^*) \in]0, \infty[^{i_*}$ and $\widehat{\kappa} = (\widehat{\kappa}_r) \in]0, \infty[^{r_*}$. Then, the quadruple $(A, B, c_*, \widehat{\kappa})$ is called a *detailed-balance reaction systems* with i_* species and r_* reactions. The associated RRE is given by (2.5).

It was observed in [Mie11] (but see also [ÖtG97, Eqn. (103)+(113)] and [Yon08, Sec. VII] for earlier, but implicit statements) that RREs in this form have a gradient structure. Here we will use the gradient structure derived in [MP*17] by a large-deviation principle from a microscopic Markov process. In Remark 2.6 we will shortly comment on other possible gradient structures.

With \mathbf{C} as above we define the energy as the relative Boltzmann entropy

$$\mathcal{E} : \begin{cases} \mathbf{C} & \rightarrow \mathbb{R}, \\ c & \mapsto \sum_{i=1}^{i_*} c_i^* \lambda_B(c_i/c_i^*), \end{cases} \quad \text{with } \lambda_B(r) = \begin{cases} r \log r - r + 1 & \text{for } r > 0, \\ 1 & \text{for } r = 0, \\ \infty & \text{for } r < 0. \end{cases} \quad (2.6a)$$

The dissipation functional \mathcal{R} will be defined by specifying the dual dissipation potential \mathcal{R}^* of “cosh-type” as

$$\mathcal{R}^* : \begin{cases} \mathbf{C} \times \mathbb{R}^{i_*} & \rightarrow \mathbb{R}, \\ (c, \xi) & \mapsto \sum_{r=1}^{r_*} \widehat{\kappa}_r \sqrt{c^{\alpha^r} c^{\beta^r}} C^*((\alpha^r - \beta^r) \cdot \xi), \end{cases} \quad \text{with } C^*(\zeta) = 4 \cosh(\zeta/2) - 4. \quad (2.6b)$$

We will often use the following formulas for C^* :

$$\begin{aligned} \text{(a) } C^*(\log p - \log q) &= 2 \frac{(\sqrt{p} - \sqrt{q})^2}{\sqrt{pq}}, \\ \text{(b) } (C^*)'(\zeta) &= e^{\zeta/2} - e^{-\zeta/2}, \quad \text{(c) } (C^*)'(\log p - \log q) = \frac{p - q}{\sqrt{pq}}. \end{aligned} \quad (2.7)$$

The following result is also easily checked by direct calculations using (2.7)(b) and the logarithm rules

$$\alpha^r D\mathcal{E}(c) = \log(c^{\alpha^r}) - \log(c_*^{\alpha^r}) = \log(c^{\alpha^r}/c_*^{\alpha^r}). \quad (2.8)$$

This identity also follows as a special case of Remark 2.6. The primal dissipation potential \mathcal{R} is given by the Legendre-Fenchel transformation:

$$\mathcal{R}(u, v) = \sup \{ \xi \cdot v - \mathcal{R}^*(c, \xi) \mid \xi \in \mathbb{R}^{i_*} \}. \quad (2.9)$$

Proposition 2.3 (Gradient structure, [MP*17, Thm. 3.6]). *The RRE (2.5) is the gradient-flow equation associated with the cosh-type gradient system $(\mathbf{C}, \mathcal{E}, \mathcal{R})$ with \mathcal{E} and \mathcal{R} given in (2.6).*

An important property of this gradient structure, which is not shared with the ones discussed in Remark 2.6 below, is that the dissipation potential \mathcal{R}^* does not depend on the equilibrium state c_* . This might seem an artifact of our special choice of the definition of $\widehat{\kappa}_r$ in terms of c_* ; however, we already see this in the example treated in Section 2.5. This property will be even more relevant when we use “tilting” in our main result Theorem 3.5, which states the “EDP-convergence with tilting”. In [MiS19, Prop. 4.1] it was shown that this tilt-invariance is a special property of the cosh-gradient structure; see also Remark 2.6.

Moreover, we have identified c_* as a “static” property of the RRE (2.5), whereas the stoichiometric matrices $A, B \in \mathbb{N}_0^{i_* \times r_*}$ and the reaction coefficients $\widehat{\kappa}_r$ encode the “dissipative” properties.

Because we are going to use the energy-dissipation principle, we explicitly state the cosh-type dissipation functional given by

$$\mathfrak{D}(c) = \int_0^T \{ \mathcal{R}(c, \dot{c}) + \mathcal{R}^*(c, -D\mathcal{E}(c)) \} dt = \int_0^T \{ \mathcal{R}(c, \dot{c}) + \mathcal{S}(c) \} dt. \quad (2.10)$$

We will mostly write the dissipation functional \mathfrak{D} in the first “ $\mathcal{R} + \mathcal{R}^*$ form” to highlight its duality structure. However, for mathematical purposes it will be advantageous to use the second representation via the *slope function*

$$\mathcal{S}(c) : \mathbf{C} \rightarrow [0, \infty[; c \mapsto \mathcal{S}(c) := \sum_{r=1}^{r_*} 2\widehat{\kappa}_r \delta_r^* \left(\left(\frac{c^{\alpha_r}}{c_*^{\alpha_r}} \right)^{1/2} - \left(\frac{c^{\beta_r}}{c_*^{\beta_r}} \right)^{1/2} \right)^2, \quad (2.11)$$

which is continuous on \mathbf{C} and satisfies $\mathcal{S}(c) = \mathcal{R}^*(c, -D\mathcal{E}(c))$ for $c \in \mathbf{C}_+$. Sometimes \mathcal{S} is also called the (discrete) Fisher information as it corresponds to $\int_{\Omega} 4k |\nabla \sqrt{\rho}|^2 dx = \int_{\Omega} k |\nabla \rho|^2 / \rho dx$ in the diffusion case.

A special feature of DBRS is that all equilibria have the property that they provide an equilibrium to each individual reaction $r \in R$, where we do not need linear independence of $(\gamma^r)_{r \in R}$, see also [MHM15, Sec. 2] or [Mie17].

Lemma 2.4 (Equilibria in DBRS). *Let $(A, B, c_*, \widehat{\kappa})$ be a DBRS with slope function \mathcal{S} defined in (2.11). Then, the following identities hold:*

$$\begin{aligned} \mathcal{E}_{\mathbf{R}} &:= \{c \in \mathbf{C} \mid \mathbf{R}(c) = 0\} = \{c \in \mathbf{C} \mid \mathcal{S}(c) = 0\} \\ &= \{c \in \mathbf{C} \mid \forall r \in R : \frac{c^{\alpha_r}}{c_*^{\alpha_r}} = \frac{c^{\beta_r}}{c_*^{\beta_r}}\}. \end{aligned} \quad (2.12)$$

Moreover, if $\tilde{c}_* \in \mathcal{E}_{\mathbf{R}} \cap \mathbf{C}_+$, then the two DBRS $(A, B, c_*, \widehat{\kappa})$ and $(A, B, \tilde{c}_*, \widehat{\kappa})$ generate the same RRE.

Proof. Step 1. For $c \in \mathbf{C}_+$ the gradient structure $\mathbf{R}(c) = \partial \mathcal{R}^*(c, -D\mathcal{E}(c))$ of the DBRS gives

$$\mathcal{R}(c, \mathbf{R}(c)) + \mathcal{R}^*(c, -D\mathcal{E}(c)) = -D\mathcal{E}(c) \cdot \mathbf{R}(c). \quad (2.13)$$

Thus, $\mathbf{R}(c) = 0$ implies $\mathcal{S}(c) = \mathcal{R}^*(c, -D\mathcal{E}(c)) = 0$, and since $\mathcal{S}(c)$ is the sum of r_* nonnegative terms (cf. (2.11)) we conclude $\frac{c^{\alpha_r}}{c_*^{\alpha_r}} = \frac{c^{\beta_r}}{c_*^{\beta_r}}$ as desired.

Step 2. If $c \in \partial \mathbf{C}$ satisfies $\mathbf{R}(c) = 0$, then consider $c_\delta = c + \delta c_* \in \mathbf{C}_+$ for $\delta \in]0, 1[$. With $|\mathbf{R}(c_\delta)| \leq C_0 \delta$, $\mathcal{R}(c_\delta, v) \geq 0$, and $|D\mathcal{E}(c_\delta)| \leq i_* \log(1/\delta)$ we find

$$\mathcal{S}(c_\delta) = \mathcal{R}^*(c_\delta, -D\mathcal{E}(c_\delta)) = -D\mathcal{E}(c_\delta) \cdot \mathbf{R}(c_\delta) - \mathcal{R}(c_\delta, \mathbf{R}(c_\delta)) \leq i_* C_0 \delta \log(1/\delta) + 0.$$

Using the continuity of \mathcal{S} we obtain $\mathcal{S}(c) = \lim_{\delta \rightarrow 0^+} \mathcal{S}(c_\delta) = 0$ and conclude as in Step 1.

Step 3. The equilibrium condition of Step 1 implies $\tilde{c}_*^{\beta_r} / \tilde{c}_*^{\alpha_r} = c_*^{\beta_r} / c_*^{\alpha_r} =: \mu_r^2$ for all $r \in R$. Because in the RRE (2.5) only the terms $\delta_*^r / c_*^{\alpha_r} = (c_*^{\beta_r} / c_*^{\alpha_r})^{1/2} = \mu_r$ and $\delta_*^r / c_*^{\beta_r} = 1/\mu_r$ appear, the last statement follows. \square

The next lemma shows that $\mathcal{R}(c, \cdot)$ forbids velocities v outside of the stoichiometric subspace Γ . Moreover, for all trajectories $c : [0, T] \rightarrow \mathbf{C}$ with $\mathfrak{D}(c) < \infty$, which are much more than the solutions of the RRE (2.1), we find that they have to lie in one stoichiometric subset \mathbf{C}_q , i.e. the conserved quantities are already encoded in \mathfrak{D} .

Below we use the characteristic function χ_A of convex analysis, which is defined via $\chi_A(v) = 0$ for $v \in A$ and $\chi_A(v) = \infty$ otherwise.

Lemma 2.5 (Conserved quantities via \mathfrak{D}). *Let Γ , Q , C_q , and \mathcal{Q} be defined as in Section 2.1, and let \mathcal{R}^* and \mathcal{R} be defined as in (2.6b) and (2.9), respectively.*

(a) *For all $(c, v) \in \mathbf{C} \times \mathbb{R}^{i^*}$ we have $\mathcal{R}(c, v) \geq \chi_\Gamma(v)$.*

(b) *If $c \in W^{1,1}([0, T]; \mathbf{C})$ satisfies $\mathfrak{D}(c) < \infty$, then $Q\dot{c} = 0$ a.e., or equivalently there exists $q \in \mathcal{Q}$ such that $c(t) \in C_q$ for all $t \in [0, T]$.*

Proof. Using $\gamma^r = \alpha^r - \beta^r$ we find $\mathcal{R}^*(c, \xi) = 0$ for $\xi \perp \Gamma = \ker(Q)$ and conclude

$$\mathcal{R}(c, v) = \sup_{\xi} (\xi \cdot v - \mathcal{R}^*(c, \xi)) \geq \sup_{\xi \perp \Gamma} (\xi \cdot v - \mathcal{R}^*(c, \xi)) = \sup_{\xi \perp \Gamma} (\xi \cdot v) = \chi_\Gamma(v).$$

This proves part (a).

The bound $\mathfrak{D}(c) < \infty$ implies that $\int_0^T \mathcal{R}(c, \dot{c}) dt < \infty$ and hence $\dot{c} \in \Gamma = \ker(Q)$ a.e. This proves $Q\dot{c}(t) = 0$ a.e. and by the absolute continuity of c , the function $t \mapsto Qc(t)$ must be constant. Hence part (b) is established as well. \square

Remark 2.6 (Different gradient structures). We emphasize that the symmetric RRE (2.5), which was obtained from the DBC, indeed has many other gradient structures with the same relative entropy \mathcal{E} given in (2.6a). Choosing arbitrary smooth and strictly convex functions $\Phi_r : \mathbb{R} \rightarrow [0, \infty[$ with $\Phi_r(0) = 0$ and $\Phi_r(-\zeta) = \Phi_r(\zeta)$ we may define

$$\mathcal{R}_{\Phi}^*(c, \xi) = \sum_{r=1}^{r^*} \widehat{\kappa}_r \delta_r^* \Lambda_r \left(\frac{c^{\alpha^r}}{c_*^{\alpha^r}}, \frac{c^{\beta^r}}{c_*^{\beta^r}} \right) \Phi_r((\alpha^r - \beta^r) \cdot \xi) \quad \text{with } \Lambda_r(a, b) = \frac{a - b}{\Phi_r'(\log a - \log b)}$$

and $\delta_r^* = (c_*^{\alpha^r} c_*^{\beta^r})^{1/2}$. Note that Λ_r can be smoothly extended by $\Lambda_r(a, a) = a/\Phi_r''(0)$.

To show that the gradient system $(\mathbf{C}, \mathcal{E}, \mathcal{R}_{\Phi})$ indeed generates (2.5) as the associated gradient-flow equation, it suffices to consider the r^{th} reaction pair, because the dual potential \mathcal{R}_{Φ}^* is additive in the reaction pairs. Inserting $D\mathcal{E}(c) = (\log(c_i/c_i^*))_{i=1, \dots, i^*}$ we obtain the relation

$$\begin{aligned} D_{\xi} \mathcal{R}_{\Phi}^*(c, -D\mathcal{E}(c)) &= \widehat{\kappa}_r \delta_r^* \Lambda_r \left(\frac{c^{\alpha^r}}{c_*^{\alpha^r}}, \frac{c^{\beta^r}}{c_*^{\beta^r}} \right) \Phi_r'((\alpha^r - \beta^r) \cdot (-D\mathcal{E}(c))) (\alpha^r - \beta^r) \\ &\stackrel{(2.8)}{=} -\widehat{\kappa}_r \delta_r^* \Lambda_r \left(\frac{c^{\alpha^r}}{c_*^{\alpha^r}}, \frac{c^{\beta^r}}{c_*^{\beta^r}} \right) \Phi_r' \left(\log \left(\frac{c^{\alpha^r}}{c_*^{\alpha^r}} \right) - \log \left(\frac{c^{\beta^r}}{c_*^{\beta^r}} \right) \right) (\alpha^r - \beta^r) = -\widehat{\kappa}_r \delta_r^* \left(\frac{c^{\alpha^r}}{c_*^{\alpha^r}} - \frac{c^{\beta^r}}{c_*^{\beta^r}} \right) (\alpha^r - \beta^r), \end{aligned}$$

which is the desired result.

The choice $\Phi_r(\zeta) = \zeta^2/2$ was used in [Mie11], while here we use $\Phi_r = C^*$ leading to

$$\Lambda_r(a, b) = (ab)^{1/2} \quad \text{and} \quad \delta_r^* \Lambda_r \left(\frac{c^{\alpha^r}}{c_*^{\alpha^r}}, \frac{c^{\beta^r}}{c_*^{\beta^r}} \right) = (c^{\alpha^r} c^{\beta^r})^{1/2}.$$

This is the desired term in (2.6b) that is independent of c_* , while for other choice of Φ_r the last term will depend on c_* (see [MiS19]).

2.4 Fast-slow reaction-rate equation

We assume that some reactions are fast with reaction coefficients $\widehat{\kappa}_r^{\varepsilon} = \kappa_r/\varepsilon$, while the others are slow with reaction coefficients $\widehat{\kappa}_r^{\varepsilon} = \kappa_r$ (of order 1). Here we assume that the set of reaction indices

$R = \{1, \dots, r_*\}$ decomposes into $R_{\text{sl}} \dot{\cup} R_{\text{fa}}$. For simplicity we assume that the detailed-balance steady state c_* is independent of ε , but a soft dependence with a limit $c_*^\varepsilon \rightarrow c_* \in \mathbf{C}_+$ could be allowed as well.

$$\begin{aligned} \dot{c} = \mathbf{R}_\varepsilon(c) &= - \sum_{r=1}^{r_*} \widehat{\kappa}_r^\varepsilon \delta_r^* \left(\frac{c^{\alpha^r}}{c_*^{\alpha^r}} - \frac{c^{\beta^r}}{c_*^{\beta^r}} \right) (\alpha^r - \beta^r) = \mathbf{R}_{\text{sl}}(c) + \frac{1}{\varepsilon} \mathbf{R}_{\text{fa}}(c) \\ \text{with } \mathbf{R}_{\text{xy}}(c) &= \sum_{r \in R_{\text{xy}}} \kappa_r \delta_r^* \left(\frac{c^{\alpha^r}}{c_*^{\alpha^r}} \frac{c^{\beta^r}}{c_*^{\beta^r}} \right) (\alpha^r - \beta^r) \quad \text{for } \text{xy} \in \{\text{sl}, \text{fa}\}. \end{aligned} \quad (2.14)$$

Obviously, for each $\varepsilon > 0$ we have a cosh-type gradient structure $(\mathbf{C}, \mathcal{E}, \mathcal{R}_\varepsilon)$ with

$$\mathcal{R}_\varepsilon^*(c, \xi) = \mathcal{R}_{\text{sl}}^*(c, \xi) + \frac{1}{\varepsilon} \mathcal{R}_{\text{fa}}^*(c, \xi) \quad \text{with } \mathcal{R}_{\text{xy}}^*(c, \xi) = \sum_{r \in R_{\text{xy}}} \kappa_r \sqrt{c^{\alpha^r} c^{\beta^r}} C^* ((\alpha^r - \beta^r) \cdot \xi). \quad (2.15)$$

The aim of this paper is to investigate the behavior of the gradient structures $(\mathbf{C}, \mathcal{E}, \mathcal{R}_\varepsilon)$ in the limit $\varepsilon \rightarrow 0^+$. In particular, we study the Γ -limit of the induced dissipation functionals \mathcal{D}_ε obtained as in (2.10) but with the duality pair $\mathcal{R}_\varepsilon + \mathcal{R}_\varepsilon^*$.

At this stage we report on well-known results (see e.g. [Bot03, DLZ18]) about the limit evolution for $\varepsilon \rightarrow 0^+$. For small times of order ε the fast system \mathbf{R}_{fa} will dominate, while for $t \in [\sqrt{\varepsilon}, T]$ a slow dynamics takes place where the slow reactions drive the evolution and the fast reactions remain in equilibrium.

To be more precise we introduce the fast time scale $\tau = t/\varepsilon$ such that in terms of τ we obtain the rescaled system $c'(\tau) = \varepsilon \mathbf{R}_{\text{sl}}(c(\tau)) + \mathbf{R}_{\text{fa}}(c(\tau))$. For $\varepsilon \rightarrow 0^+$ we obtain the fast system

$$c'(\tau) = \mathbf{R}_{\text{fa}}(c(\tau)), \quad c(0) = c_0. \quad (2.16)$$

This is again a RRE satisfying the detailed-balance condition and all constructions introduced in Sections 2.1 and 2.3. In particular we obtain the fast stoichiometric subspace

$$\Gamma_{\text{fa}} := \text{span} \{ \gamma^r \in \mathbb{Z}^{i_*} \mid r \in R_{\text{fa}} \} \subset \Gamma \subset \mathbb{R}^{i_*}.$$

For the annihilator $\Gamma_{\text{fa}}^\perp := \{ q \in \mathbb{R}^{i_*} \mid \forall \gamma \in \Gamma_{\text{fa}} : q \cdot \gamma = 0 \}$ we have $\Gamma^\perp \subset \Gamma_{\text{fa}}^\perp$ and $m_{\text{fa}} := \dim \Gamma_{\text{fa}}^\perp \geq m = \dim \Gamma^\perp$. Thus, we can extend the basis $\{q_1, \dots, q_m\}$ for Γ^\perp to a basis $\{q_1, \dots, q_m, \dots, q_{m_{\text{fa}}}\}$ for Γ_{fa}^\perp and define the conservation operator $Q_{\text{fa}} : \mathbb{R}^{i_*} \rightarrow \mathbb{R}^{m_{\text{fa}}}$ via

$$Q_{\text{fa}}^\top := (q_1, \dots, q_{m_{\text{fa}}}) : \mathbb{R}^{m_{\text{fa}}} \rightarrow \mathbb{R}^{i_*} \quad \text{and set } \mathbf{Q} := \{ Q_{\text{fa}} c \in \mathbb{R}^{m_{\text{fa}}} \mid c \in \mathbf{C} \}.$$

In particular, the important defining relations of Q_{fa} are

$$\ker Q_{\text{fa}} = \Gamma_{\text{fa}} \quad \text{and} \quad \text{im } Q_{\text{fa}}^\top = \Gamma_{\text{fa}}^\perp. \quad (2.17)$$

Of course, our interest lies in the case $0 \leq m \leq m_{\text{fa}} \leq i_*$. In that case the mapping $c \mapsto Qc$ yields fewer conserved quantities for the full fast-slow RRE (2.14) than the mapping $c \mapsto \mathbf{q} = Q_{\text{fa}}c$ supplies for the fast RRE (2.16). We call $\mathbf{q} \in \mathbf{Q}$ the slow variables, as they may still vary on the slow time scale. In particular, the decomposition of \mathbf{C} into fast stoichiometric subsets

$$\mathbf{C} = \bigcup_{\mathbf{q} \in \mathbf{Q}} \mathbf{C}_{\mathbf{q}}^{\text{fa}} \quad \text{where} \quad \mathbf{C}_{\mathbf{q}}^{\text{fa}} := \{ c \in \mathbf{C} \mid Q_{\text{fa}}c = \mathbf{q} \} \quad (2.18)$$

is finer than $\mathbf{C} = \bigcup_{q \in \mathcal{Q}} \mathbf{C}_q$.

Starting from a general initial condition c_0 , one can show that the solutions $c^\varepsilon : [0, T] \rightarrow \mathbf{C}$ of the fast-slow RRE (2.14) have a limit $c^0 : [0, T] \rightarrow \mathbf{C}$, but this limit may not be continuous at $t = 0$. On the short time scale $\tau = t/\varepsilon$ we may define $\tilde{c}^\varepsilon(\tau) = c^\varepsilon(\varepsilon\tau)$ which has a limit $\tilde{c}^0 : [0, \infty[\rightarrow \mathbf{C}$ satisfying the fast RRE (2.16) and having a limit $\bar{c}_0 := \lim_{\tau \rightarrow \infty} \tilde{c}^0(\tau)$ with $\mathbf{R}_{\text{fa}}(\bar{c}_0) = 0$. Hence, we define the set of fast equilibria

$$\mathcal{E}_{\text{fa}} := \{c \in \mathbf{C} \mid \mathbf{R}_{\text{fa}}(c) = 0\} = \{c \in \mathbf{C} \mid \forall r \in R_{\text{fa}} : \frac{c^{\alpha_r}}{c_*^{\alpha_r}} = \frac{c^{\beta_r}}{c_*^{\beta_r}}\} \quad (2.19)$$

such that for $\tau \in [0, \infty[$ the solution $\tilde{c}^0(\tau)$ describes the approach to the slow manifold and $\bar{c}_0 \in \mathcal{E}_{\text{fa}}$. On the time scale of order 1, the limits $c^0(t)$ of the solutions $c^\varepsilon(t)$ satisfy $c^0(t) \in \mathcal{E}_{\text{fa}}$ for all $t \in]0, T]$, and one has the matching condition $\bar{c}_0 = \lim_{t \rightarrow 0^+} c^0(t)$.

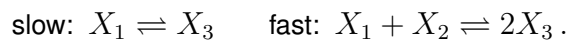
The evolution of the solutions c^0 within \mathcal{E}_{fa} is driven by the slow reactions only; the fast reactions keep the solution on the fast-equilibrium manifold \mathcal{E}_{fa} . In particular, it can be shown (see [Bot03, DLZ18] or [MIS19] for the linear case) that c^0 satisfies the limiting equation

$$\dot{c}(t) = \mathbf{R}_{\text{sl}}(c(t)) + \lambda(t) \quad \text{with } c(t) \in \mathcal{E}_{\text{fa}} \text{ and } \lambda(t) \in \Gamma_{\text{fa}}, \quad c(0) = \bar{c}_0. \quad (2.20)$$

The result of our paper is quite different: We will pass to the limit in the gradient systems $(\mathbf{C}, \mathcal{E}, \mathcal{R}_\varepsilon)$ directly and obtain an effective gradient system $(\mathbf{C}, \mathcal{E}, \mathcal{R}_{\text{eff}})$, see Theorem 3.5. As a consistency check, we will show in Section 4 that the gradient-flow equation for $(\mathbf{C}, \mathcal{E}, \mathcal{R}_{\text{eff}})$ is indeed identical to the limiting equation (2.20), see Proposition 4.4.

2.5 A simple example for a fast-slow system

As a guiding example, we consider a reaction system consisting of three species $X_i, i = 1, 2, 3 = i_*$, which interact via $r_* = 2$ reactions, one being slow and one being fast:



Hence, the stoichiometric vector are given by

$$\begin{aligned} \alpha^1 &= (1, 0, 0)^\top, & \beta^1 &= (0, 0, 1)^\top, & \gamma^1 &= (1, 0, -1)^\top, \\ \alpha^2 &= (1, 1, 0)^\top, & \beta^2 &= (0, 0, 2)^\top, & \gamma^2 &= (1, 1, -2)^\top. \end{aligned}$$

Hence, one can easily check that the space of conserved quantities is $\text{span}((1, 1, 1)^\top) \in \mathbb{R}^3$ which defines the matrix $Q = (1, 1, 1) \in \mathbb{R}^{1 \times 3}$.

We have $R = R_{\text{fa}} \cup R_{\text{sl}} = \{1\} \cup \{2\}$ and the RRE reads

$$\dot{c} = \mathbf{R}_\varepsilon(c) = (c_3 - 3c_1) \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} + \frac{1}{\varepsilon} (c_3^2 - c_1 c_2) \begin{pmatrix} 1 \\ 1 \\ -2 \end{pmatrix}. \quad (2.21)$$

The nontrivial equilibria of this RRE are given by $c_* = (c_1^*, c_2^*, c_3^*)^\top = \sigma(1, 9, 3)^\top$ for $\sigma > 0$. All these c_* satisfy the detailed balance condition, and (2.21) takes the symmetric form (2.5), viz.

$$\begin{aligned} \dot{c} &= -\kappa_1 \delta_1^* \left(\frac{c_1}{c_1^*} - \frac{c_3}{c_3^*} \right) \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} - \frac{\kappa_2}{\varepsilon} \delta_2^* \left(\frac{c_1 c_2}{c_1^* c_2^*} - \frac{c_3^2}{(c_3^*)^2} \right) \begin{pmatrix} 1 \\ 1 \\ -2 \end{pmatrix} \\ \text{with } \delta_1^* &= (c_1^* c_3^*)^{1/2} = \sigma \sqrt{3}, \quad \delta_2^* = (c_1^* c_2^*)^{1/2} c_3 = 9\sigma^2, \quad \kappa_1 = \sqrt{3}, \quad \text{and } \kappa_2 = 1. \end{aligned}$$

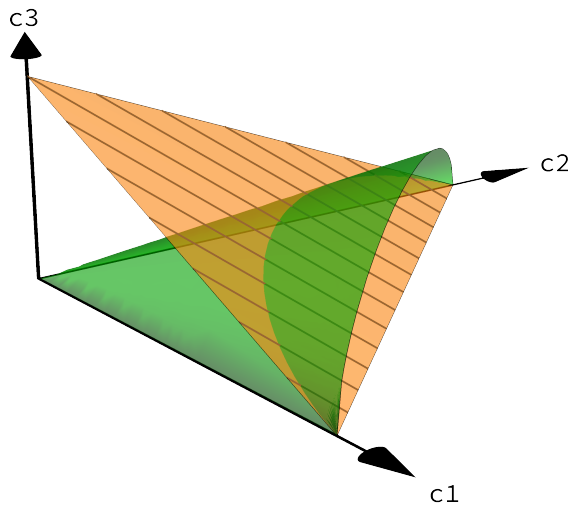


Figure 2.1: The state space $\mathbf{C} = [0, \infty[{}^3$ decomposes into the triangles $Qc = c_1 + c_2 + c_3 = q$ (light brown), which decompose into the straight segments $Q_{\text{fa}}c = q$ (brown). Each segment has exactly one intersection with the fast equilibria \mathcal{E}_{fa} (green).

Thus, we find the cosh-type gradient structure $(\mathbf{C}, \mathcal{E}, \mathcal{R}_\varepsilon^*)$ of Section 2.3 with

$$\begin{aligned} \mathcal{E}(c) &= \sigma \lambda_B(c_1/\sigma) + 9\sigma \lambda_B(c_2/(9\sigma)) + 3\sigma \lambda_B(c_3/(3\sigma)), \\ \mathcal{R}_\varepsilon^*(c, \xi) &= \sqrt{3c_1c_3} \mathbf{C}^*(\xi_1 - \xi_3) + \frac{1}{\varepsilon} \sqrt{c_1c_2c_3^2} \mathbf{C}^*(\xi_1 + \xi_2 - 2\xi_3). \end{aligned}$$

As noted just after Proposition 2.3, $\mathcal{R}_\varepsilon^*$ is independent of c_* .

The associated fast system consists simply of one reaction, hence we find

$$\Gamma_{\text{fa}} = \text{span}(1, 1, -2)^\top, \quad Q_{\text{fa}} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & -1 & 0 \end{pmatrix}, \quad \mathbf{Q} = \{ \mathbf{q} \in \mathbb{R}^2 \mid q_1 \geq 0 \}.$$

The stoichiometric sets \mathbf{C}_q with $Qc = q \in \mathbb{R}^1$ are triangles, which decompose into the straight segments \mathbf{C}_q^{fa} given by $Q_{\text{fa}}c = q$, whereas the set of fast equilibria

$$\mathcal{E}_{\text{fa}} = \{ c \in \mathbf{C} \mid c_1c_2 = c_3^2 \}.$$

is curved. See Figure 2.5 for an illustration.

Finally, we discuss the evolution for our example starting with the initial condition $c_0 = (10, 4, 0)^\top$ such that $Qc^\varepsilon(t) = c_1^\varepsilon(t) + c_2^\varepsilon(t) + c_3^\varepsilon(t) = 14$ is the conserved quantity. Since there is only one fast reaction, the second conserved quantity $c_1 - c_2 = q_2 = 6$ shows that $\tilde{c}^\varepsilon(\tau) = c^\varepsilon(\varepsilon\tau)$ converges to $\tilde{c}(\tau)$ and $\tilde{c}(\tau) \rightarrow \bar{c}_0 = (8, 2, 4)^\top \in \mathcal{E}_{\text{fa}}$ for $\tau \rightarrow \infty$.

Thus, the limit solution c^0 satisfies the limiting equation (2.20), which reads in our case

$$\dot{c} = (c_3 - 3c_1) \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} + \lambda_0 \begin{pmatrix} 1 \\ 1 \\ -2 \end{pmatrix}, \quad c_1(t)c_2(t) = c_3(t)^2, \quad c(0) = \bar{c}_0 = (8, 2, 4)^\top.$$

By eliminating the Lagrange multiplier $\lambda_0 \in \mathbb{R}$ and using the conserved quantity $Qc = 14$ this system is equivalent to the system

$$\dot{c}_1 - \dot{c}_2 = c_3 - 3c_1, \quad c_1c_2 = c_3^2, \quad c_1 + c_2 + c_3 = 14.$$

Simulations are shown in Figure 2.5, which show the fast convergence to \mathcal{E}_{fa} and then the slow convergence to the final steady state $c_{\text{eq}} = (1, 9, 4)^\top$.

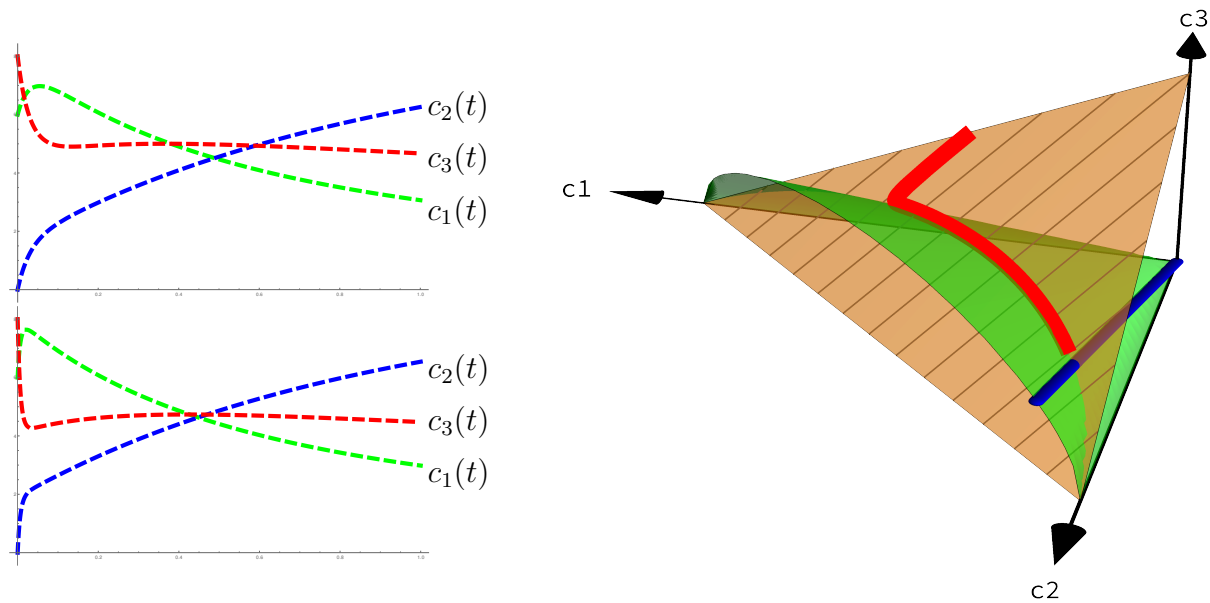


Figure 2.2: Numerical calculation of the solutions $c^\varepsilon(t)$ for the RRE (2.21) with $c^\varepsilon(0) = (4, 0, 10)^\top$ with $\varepsilon = 1$ (upper left) and $\varepsilon = 0.2$ (lower left). The lower left figure shows the fast convergence to $\bar{c}_0 = (8, 2, 4)^\top$. The right graphs displays the curve $t \mapsto c^\varepsilon(t)$ (red), which lies in the plane $QC = 14$ (light brown). It quickly approaches \mathcal{M}_{sl} (green) and then moves towards the set of steady states (blue).

3 EDP-convergence and effective gradient structure

In this section we first provide the precise definitions of EDP-convergence for gradient systems. Next we present our main result concerning the EDP-limit of the cosh-type gradient structure for the fast-slow RRE with detailed-balance condition as introduced in Section 2.4, where the proofs are postponed to later sections. Finally, in Section 4 we discuss the obtained effective gradient system $(\mathbf{C}, \mathcal{E}, \mathcal{R}_{\text{eff}})$ and show that the induced gradient-flow equation indeed is the same as the limiting equation (2.20).

3.1 Definition of different types of EDP-convergence

The definition of EDP-convergence for gradient systems relies on the notion of Γ -convergence for functionals (cf. [Dal93]). If Y is a Banach space and $I_\varepsilon : Y \rightarrow \mathbb{R}_\infty$ we write $I_\varepsilon \xrightarrow{\Gamma} I_0$ and $I_\varepsilon \xrightarrow{\Gamma} I_0$ for Γ -convergence in the strong and weak topology, respectively. If both holds this is called Mosco convergence and written as $I_\varepsilon \xrightarrow{M} I_0$.

For families of gradient systems $(X, \mathcal{E}_\varepsilon, \mathcal{R}_\varepsilon)$, three different levels of EDP-convergence are introduced and discussed in [DFM19, MMP19], called simple EDP-convergence, EDP-convergence with tilting, and contact EDP-convergence with tilting. Here we will only use the first two notions. For all three notions the choice of weak or strong topology is still to be decided according to the specific problem. Here in the state space $X = \mathbb{R}^{i^*}$ this question is irrelevant, but it is relevant for curves $u : [0, T] \rightarrow \mathbf{X}$ lying in $Y = L^1([0, T]; X)$, where the state space \mathbf{X} is a closed convex subset with non-empty interior of the Banach space X . For our paper, the strong topology will be sufficient.

Definition 3.1 (Simple EDP-convergence). A family of gradient structures $(\mathbf{X}, \mathcal{E}_\varepsilon, \mathcal{R}_\varepsilon)$ is said to *EDP-*

converge to the gradient system $(\mathbf{X}, \mathcal{E}_0, \mathcal{R}_{\text{eff}})$ if the following conditions hold:

- 1) $\mathcal{E}_\varepsilon \xrightarrow{\Gamma} \mathcal{E}_0$ on $\mathbf{X} \subset X$;
- 2) \mathfrak{D}_ε strongly Γ -converges to \mathfrak{D}_0 on $L^1([0, T]; \mathbf{X})$ conditioned to bounded energies (we write $\mathfrak{D}_\varepsilon \xrightarrow{\Gamma_E} \mathfrak{D}_0$), i.e. we have
 - 2a) (Liminf) For all strongly converging families $u_\varepsilon \rightarrow u$ in $L^1([0, T]; \mathbf{X})$ which satisfy $\sup_{\varepsilon > 0} \text{ess sup}_{t \in [0, T]} \mathcal{E}_\varepsilon(u_\varepsilon(t)) < \infty$, we have $\liminf_{\varepsilon \rightarrow 0^+} \mathfrak{D}_\varepsilon(u_\varepsilon) \geq \mathfrak{D}_0(u)$.
 - 2b) (Limsup) For all $\tilde{u} \in L^1([0, T]; \mathbf{X})$ there exists a strongly converging family $\tilde{u}_\varepsilon \rightarrow \tilde{u}$ in $L^1([0, T]; \mathbf{X})$ with $\sup_{\varepsilon > 0} \text{ess sup}_{t \in [0, T]} \mathcal{E}_\varepsilon(\tilde{u}_\varepsilon(t)) < \infty$ and $\limsup_{\varepsilon \rightarrow 0^+} \mathfrak{D}_\varepsilon(\tilde{u}_\varepsilon) \leq \mathfrak{D}_0(\tilde{u})$;
- 3) there is an effective dissipation potential $\mathcal{R}_{\text{eff}} : \mathbf{X} \times X \rightarrow \mathbb{R}_\infty$ such that \mathfrak{D}_0 takes the form of a dual sum, namely $\mathfrak{D}_0(u) = \int_0^T \{\mathcal{R}_{\text{eff}}(u, \dot{u}) + \mathcal{R}_{\text{eff}}^*(u, -D\mathcal{E}_{\text{eff}}(u))\} dt$.

Similarly, one can also use weak Γ or Mosco convergence conditioned to bounded energy, which we will then write as $\mathfrak{D}_\varepsilon \xrightarrow{\Gamma_E} \mathfrak{D}_0$ and $\mathfrak{D}_\varepsilon \xrightarrow{M_E} \mathfrak{D}_0$. In fact, for our fast-slow reaction systems we are going to prove $\mathfrak{D}_\varepsilon \xrightarrow{M_E} \mathfrak{D}_0$.

A general feature of EDP-convergence is that under suitable conditions the gradient-flow equation $\dot{u} = \partial_\xi \mathcal{R}_{\text{eff}}^*(u, -D\mathcal{E}_0(u))$ of the effective gradient system $(X, \mathcal{E}_0, \mathcal{R}_{\text{eff}})$ is indeed the limiting equation for the family $\dot{u} = \partial_\xi \mathcal{R}_\varepsilon^*(u, -D\mathcal{E}_\varepsilon(u))$, i.e. limits u^0 of solutions u^ε of latter equations solve the former equation, see e.g. [Bra14, Thm. 11.3], [MiS19, Lem. 3.4], or [MMP19, Lem. 2.8]. For our case, such a result is given in Propositions 4.3 and 4.4.

A strengthening of simple EDP-convergence is the so-called *EDP-convergence with tilting*. This notion involves the tilted energy functionals $\mathcal{E}_\varepsilon^\eta : \mathbf{X} \ni u \mapsto \mathcal{E}_\varepsilon(u) - \langle \eta, u \rangle$, where the tilt η (also called forcing) varies through the whole dual space X^* .

Definition 3.2 (EDP-convergence with tilting (cf. [MMP19, Def. 2.14])). A family of gradient structures $(\mathbf{X}, \mathcal{E}_\varepsilon, \mathcal{R}_\varepsilon)$ is said to *EDP-converge with tilting* to the gradient system $(\mathbf{X}, \mathcal{E}_0, \mathcal{R}_{\text{eff}})$, if for all tilts $\eta \in X^*$ we have $(\mathbf{X}, \mathcal{E}_\varepsilon^\eta, \mathcal{R}_\varepsilon)$ EDP-converges to $(\mathbf{X}, \mathcal{E}_0^\eta, \mathcal{R}_{\text{eff}})$.

We observe that $\mathcal{E}_\varepsilon \xrightarrow{\Gamma} \mathcal{E}_0$ implies $\mathcal{E}_\varepsilon^\eta \xrightarrow{\Gamma} \mathcal{E}_0^\eta$ for all $\eta \in X^*$ (and similarly for weak Γ -convergence), since the linear tilt $u \mapsto -\langle \eta, u \rangle$ is weakly continuous. The main and nontrivial assumption is that additionally

$$\mathfrak{D}_\varepsilon^\eta : u \mapsto \int_0^T \{\mathcal{R}_\varepsilon(u, \dot{u}) + \mathcal{R}_\varepsilon^*(u, \eta - D\mathcal{E}_\varepsilon(u))\} dt$$

Γ -converges in $L^1([0, T]; \mathbf{X})$ to \mathfrak{D}_0^η for all $\eta \in X^*$ and that this limit \mathfrak{D}_0^η is given in dual-sum form with \mathcal{R}_{eff} via

$$\mathfrak{D}_0^\eta(u) = \int_0^T \{\mathcal{R}_{\text{eff}}(u, \dot{u}) + \mathcal{R}_{\text{eff}}^*(u, \eta - D\mathcal{E}_{\text{eff}}(u))\} dt.$$

The main point is that \mathcal{R}_{eff} remains independent of $\eta \in X^*$. We refer to [MMP19] for a discussion of this and the other two notions of EDP-convergence.

3.2 Our main EDP-convergence result

Since we have assumed that the stationary measure does not depend on $\varepsilon > 0$, also the energy $\mathcal{E}_\varepsilon = \mathcal{E}$ is ε -independent. Since \mathcal{E} is also convex and lower semicontinuous, we have the trivial Mosco convergence $\mathcal{E}_\varepsilon \xrightarrow{M} \mathcal{E}$.

To study the Γ -limit of the dissipation functionals \mathfrak{D}_ε we first extend them to the space

$$L^1([0, T]; \mathbf{C}) := \{ c \in L^1([0, T]; \mathbb{R}^{i_*}) \mid c(t) \in \mathbf{C} \text{ a.e. } \}.$$

For this we also use the slope functions (where $xy \in \{\text{fa}, \text{sl}\}$)

$$\mathcal{S}_\varepsilon(c) = \mathcal{S}_{\text{sl}}(c) + \frac{1}{\varepsilon} \mathcal{S}_{\text{fa}}(c) \quad \text{with } \mathcal{S}_{xy}(c) = \sum_{r \in R_{xy}} 2\kappa_r \delta_r^* \left(\left(\frac{c^{\alpha^r}}{c_*^{\alpha^r}} \right)^{1/2} - \left(\frac{c^{\beta^r}}{c_*^{\beta^r}} \right)^{1/2} \right)^2. \quad (3.1)$$

For $\varepsilon > 0$ the dissipation functional $\mathfrak{D}_\varepsilon : L^1([0, T]; \mathbf{C}) \rightarrow [0, \infty]$ is now given by

$$\mathfrak{D}_\varepsilon(c) = \begin{cases} \int_0^T \{ \mathcal{R}_\varepsilon(c, \dot{c}) + \mathcal{S}_\varepsilon(c) \} dt & \text{for } c \in W^{1,1}([0, T]; \mathbf{C}), \\ \infty & \text{otherwise.} \end{cases} \quad (3.2)$$

We recall that the dual dissipation potentials are given by (with $\gamma^r = \alpha^r - \beta^r$)

$$\mathcal{R}_\varepsilon^*(c, \xi) = \mathcal{R}_{\text{sl}}^*(c, \xi) + \frac{1}{\varepsilon} \mathcal{R}_{\text{fa}}^*(c, \xi) \quad \text{with } \mathcal{R}_{xy}^*(c, \xi) = \sum_{r \in R_{xy}} \kappa_r \sqrt{c^{\alpha^r} c^{\beta^r}} C^*(\gamma^r \cdot \xi).$$

Because $\mathcal{S}_{\text{fa}}(c) \geq 0$ and $\mathcal{R}_{\text{fa}}^*(c, \xi) \geq 0$ we observe that $\mathcal{S}_\varepsilon(c)$ and $\mathcal{R}_\varepsilon^*(c, \xi)$ are monotonously increasing for $\varepsilon \downarrow 0$. Thus, their Γ -limits exist and are equal to the pointwise limits, which are denoted by \mathcal{S}_0 and \mathcal{R}_0^* respectively (this uses [Dal93, Rem. 5.5] and the continuity of \mathcal{S}_{fa} and $\mathcal{R}_{\text{fa}}^*$.)

Using (2.12) for the fast system we know that for $c \in \mathbf{C}$ the three conditions $\mathbf{R}_{\text{fa}}(c) = 0$, $\mathcal{S}_{\text{fa}}(c) = 0$, and $c \in \mathcal{E}_{\text{fa}}^\circ$ are equivalent. Hence, we conclude

$$\lim_{\varepsilon \rightarrow 0^+} \mathcal{S}_\varepsilon(c) =: \mathcal{S}_0(c) = \mathcal{S}_{\text{sl}}(c) + \chi_{\mathcal{E}_{\text{fa}}^\circ}(c), \quad \text{where } \chi_A(b) = \begin{cases} 0 & \text{for } b \in A, \\ \infty & \text{for } b \notin A. \end{cases}$$

Obviously, we have $\lim_{\varepsilon \rightarrow 0^+} \mathcal{R}_\varepsilon^*(c, \xi) =: \mathcal{R}_0^*(c, \xi) = 0$ for $\xi \in \Gamma_{\text{fa}}^\perp$ and for $c \in \mathbf{C}_+$ we obtain $\mathcal{R}_0^*(c, \xi) = \infty$ for $\xi \notin \Gamma_{\text{fa}}^\perp$. Thus, we define the effective dual dissipation potential as

$$\mathcal{R}_{\text{eff}}^*(c, \xi) = \mathcal{R}_{\text{sl}}^*(c, \xi) + \chi_{\Gamma_{\text{fa}}^\perp}(\xi). \quad (3.3)$$

Note that $\mathcal{R}_{\text{eff}}^*(c, \xi) \geq \mathcal{R}_0^*(c, \xi)$ where inequality may happen on the boundary of \mathbf{C} , e.g. at $c = 0$. Nevertheless, we have the important relation

$$\forall c \in \mathbf{C}_+ : \mathcal{R}_{\text{eff}}^*(c, -D\mathcal{E}(c)) = \mathcal{S}_0(c) := \mathcal{S}_{\text{sl}}(c) + \chi_{\mathcal{E}_{\text{fa}}^\circ}(c). \quad (3.4a)$$

The primal effective dissipation potential \mathcal{R}_{eff} is given by the Legendre–Fenchel transformation:

$$\begin{aligned} \mathcal{R}_{\text{eff}}(c, v) &= \sup_{\xi \in \mathbb{R}^{i_*}} \{ v \cdot \xi - \mathcal{R}_{\text{eff}}^*(c, \xi) \} = \sup_{\xi \in \mathbb{R}^{i_*}} \left\{ v \cdot \xi - \mathcal{R}_{\text{sl}}^*(c, \xi) - \chi_{\Gamma_{\text{fa}}^\perp}(\xi) \right\} \\ &= \inf_{v_1 + v_2 = v} \{ \mathcal{R}_{\text{sl}}(c, v_1) + \chi_{\Gamma_{\text{fa}}}(v_2) \} = \inf_{v_2 \in \Gamma_{\text{fa}}} \{ \mathcal{R}_{\text{sl}}(c, v - v_2) \}, \end{aligned} \quad (3.4b)$$

where we have used $(\chi_{\Gamma_{\text{fa}}})^* = \chi_{\Gamma_{\text{fa}}^\perp}$ and the classical theorem on the Legendre-Fenchel transformation turning a sum into an infimal convolution (see [Att84, Prop. 3.4]).

To state our main result we now impose a non-trivial structural assumption that is crucial for our result and its proof. An analogous condition on the uniqueness of equilibria in each stoichiometric subset \mathbf{C}_q^{fa} was used in [Mie17, Eqn. (17)]. We believe that the theory of EDP-convergence can be studied without this assumption, but then one has to refine the results and the solution technique suitably, see the counterexample in Remark 3.10.

Assumption 3.3 (Conditions on the fast equilibria \mathcal{E}_{fa}). *For all $q \in \mathbf{Q} := \{Q_{\text{fa}}c \mid c \in \mathbf{C}\}$, there is exactly one equilibrium of $c' = \mathbf{R}_{\text{fa}}(c)$ in the invariant subset \mathbf{C}_q^{fa} (cf. (2.18)), i.e.*

$$(UFEC) \quad \forall q \in \mathbf{Q} : \#(\mathbf{C}_q^{\text{fa}} \cap \mathcal{E}_{\text{fa}}) = 1, \quad (3.5)$$

which is called the unique fast-equilibrium condition. By $\Psi : \mathbf{Q} \rightarrow \mathbf{C}$ we denote the mapping such that $\{\Psi(q)\} = \mathbf{C}_q^{\text{fa}} \cap \mathcal{E}_{\text{fa}}$ for all $q \in \mathbf{Q}$.

We further impose the following positivity assumption on Ψ :

$$\exists \bar{q} \in \mathbf{Q} \forall \theta \in]0, 1] \forall q \in \mathbf{Q} \forall i \in I : \Psi(q + \theta \bar{q})_i > 0 \text{ and } \Psi(q + \theta \bar{q})_i \geq \Psi(q)_i. \quad (3.6)$$

The positivity and monotonicity assumption (3.6) seems to be only technical and it is only used at one point, namely in Step 1 in the proof of Theorem 5.5. We expect that this assumption can be avoided by a more careful construction of recovery sequence.

In Section 3.3 we will show that one of possibly several equilibria in \mathbf{C}_q^{fa} is always given as the minimizer of \mathcal{E} on \mathbf{C}_q^{fa} . Thus, the assumption really means that this ‘‘thermodynamic equilibrium’’ is the only steady state. Our main Γ -convergence result reads as follows.

Theorem 3.4 (Γ -convergence). *Consider a fast-slow DBRS $(A, B, c_*, \widehat{\kappa}^\varepsilon)$ as in (2.14) together with its cosh-type gradient structure $(\mathbf{C}, \mathcal{E}, \mathcal{R}_\varepsilon)$ as in Proposition 2.3 and the dissipation functional \mathcal{D}_ε defined in (3.2). Moreover, let Assumption 3.3 be satisfied.*

Then we have $\mathcal{D}_\varepsilon \xrightarrow{M_E} \mathcal{D}_0$ on $L^1([0, T], \mathbf{C})$ conditioned to bounded energies, where the functional $\mathcal{D}_0 : L^1([0, T]; \mathbf{C}) \rightarrow [0, \infty]$ is defined as

$$\mathcal{D}_0(c) := \begin{cases} \int_0^T \{\mathcal{R}_{\text{eff}}(c, \dot{c}) + \mathcal{S}_0(c)\} dt & \text{for } c \in C^0([0, T]; \mathbf{C}) \text{ and } Q_{\text{fa}}c \in W^{1,1}([0, T]; \mathbb{R}^{m_{\text{fa}}}), \\ \infty & \text{otherwise,} \end{cases}$$

where \mathcal{R}_{eff} and \mathcal{S}_0 are defined in (3.4).

The proof of this result is the content of Section 5.

We emphasize that the integrand of \mathcal{D}_0 is (i) degenerate (non-coercive) in \dot{c} and (ii) singular (taking the value ∞). Concerning (i), we recall that the definition of \mathcal{R}_{eff} in (3.4b) implies that $\mathcal{R}_{\text{eff}}(c, \cdot)$ vanishes on Γ_{fa} . In fact, it is only possible to control the time derivative of $t \mapsto Q_{\text{fa}}c(t) \in \mathbb{R}^{m_{\text{fa}}}$. Concerning (ii), we observe that \mathcal{S}_0 equals $+\infty$ outside of \mathcal{E}_{fa} , which is a manifold of dimension m_{fa} , and at each $c \in \mathcal{E}_{\text{fa}} \cap \mathbf{C}_+$ the subspaces $\mathbb{T}_c \mathcal{E}_{\text{fa}}$ and Γ_{fa} are transversal, see Section 4. Assumption 3.3 will be needed to avoid jump-type behavior which can occur otherwise, see the counterexample discussed in Remark 3.10.

We now come to our main result on the EDP-convergence with tilting for the cosh-type gradient systems $(\mathbf{C}, \mathcal{E}, \mathcal{R}_\varepsilon)$ towards the effective gradient system $(\mathbf{C}, \mathcal{E}, \mathcal{R}_{\text{eff}})$.

The theorem enables to establish our main result on EDP-convergence with tilting. The result is a direct consequence of the Γ -convergence stated in Theorem 3.4 and the general fact for the Boltzmann entropy that tilting is equivalent to changing the reference measure. In fact, introducing the relative Boltzmann entropy $\mathcal{H}(c|w) = \sum_{i=1}^{i_*} w_i \lambda_B(c_i/w_i)$ we have $\mathcal{E}(c) = \mathcal{H}(c|c_*)$ and obtain, for all $\eta \in \mathbb{R}^{i_*}$, the relation

$$\mathcal{E}^\eta(c) = \mathcal{E}(c) - \eta \cdot c = \mathcal{H}(c|\mathbb{D}^\eta c_*) + E_\eta \quad \text{with } \mathbb{D}^\eta c := (e^{\eta_i} c_i)_{i \in I} \text{ and } E_\eta = \sum_{i=1}^{i_*} (1 - e^{\eta_i}) c_i^*. \quad (3.7)$$

Thus, we observe that tilting of a DBRS $(A, B, c_*, \widehat{\kappa}^\varepsilon)$ only changes the static property, namely the equilibrium c_* into $\mathbb{D}^\eta c_*$, while the dissipative properties encoded in the stoichiometric matrices A and B and the reaction coefficients $\widehat{\kappa}$ remain unchanged.

Theorem 3.5 (EDP-convergence with tilting). *Under the assumptions of Theorem 3.4, the gradient systems $(\mathbf{C}, \mathcal{E}, \mathcal{R}_\varepsilon)$ EDP-converge with tilting to the gradient system $(\mathbf{C}, \mathcal{E}, \mathcal{R}_{\text{eff}})$.*

Proof. Step 1. Simple EDP-convergence: Since $\mathcal{E}_\varepsilon = \mathcal{E}$ is continuous we obviously have $\mathcal{E}_\varepsilon \xrightarrow{M} \mathcal{E}$. Moreover, Theorem 3.4 provides $\mathcal{D}_\varepsilon \xrightarrow{M_E} \mathcal{D}_0$. Finally, the relation (3.4a) shows that the integrand of \mathcal{D}_0 has the desired dual structure $\mathcal{R}_{\text{eff}}(c, \dot{c}) + \mathcal{R}_{\text{eff}}^*(c, -D\mathcal{E}(c))$. Thus, we have established the simple EDP-convergence of $(\mathbf{C}, \mathcal{E}, \mathcal{R}_\varepsilon)$ to the effective gradient system $(\mathbf{C}, \mathcal{E}, \mathcal{R}_{\text{eff}})$.

Step 2. EDP-convergence with tilting: We use that $\mathcal{E}^\eta = \mathcal{H}(\cdot|\mathbb{D}^\eta c_*) + E_\eta$ is of the same type as $\mathcal{E} = \mathcal{H}(\cdot|c_*)$ if we ignore the irrelevant constant energy shift. Clearly, the new fast-slow RRE (2.14) has the same A, B, κ_r, i_* , and hence Q_{fa} ; only c_* is replaced by $\mathbb{D}^\eta c_*$. Thus, all structural assumptions are the same, and Theorem 3.4 is applicable for all $\eta \in \mathbb{R}^{i_*}$. In particular, the UFEC in (3.5) holds for the tilted DBRS by Corollary 3.8. Thus, $(\mathbf{C}, \mathcal{E}^\eta, \mathcal{R}_\varepsilon)$ EDP-converges to $(\mathbf{C}, \mathcal{E}^\eta, \mathcal{R}_{\text{eff}})$ according to Step 1. Since the effective dissipation potential \mathcal{R}_{eff} is independent of $\eta \in \mathbb{R}^{i_*}$, we have shown EDP-convergence with tilting. \square

3.3 Discussion of the UFEC and definition of \mathcal{M}_{sl}

Here we first prove properties of the function Ψ that provides the fast equilibria (see Assumption 3.3). Secondly, we show that UFEC is invariant under tilting.

The stoichiometric subsets $\mathbf{C}_q^{\text{fa}} := \{c \in \mathbf{C} \mid Q_{\text{fa}} c = q\}$ are the intersection of the affine subspace $\{y \in \mathbb{R}^{i_*} \mid Q_{\text{fa}} y = q\}$ of dimension m_{fa} with the simplicial convex cone $\mathbf{C} = [0, \infty]^{i_*}$. Hence, each \mathbf{C}_q^{fa} is a closed and convex simplex of dimension $m(q) \in \{0, 1, \dots, m_{\text{fa}}\}$. The simplex-boundary $\partial \mathbf{C}_q^{\text{fa}}$ of such a simplex is the union of its boundary simplices of dimension $m(q) - 1$. A two-dimensional n -gon has n intervals as boundary, and an interval has 2 points as boundary. For the case of a point, which is the only 0-dimensional simplex, we say that the boundary is empty. We say that an equilibrium $c \in \mathcal{E}_{\text{fa}}^o$ is a *boundary equilibrium* if $c \in \partial \mathbf{C}_q^{\text{fa}}$. Otherwise $c \in \mathcal{E}_{\text{fa}}^o$ is called an *interior equilibrium*.

The following result provides an alternative construction of the mapping $\Psi : \mathbf{Q} \rightarrow \mathbf{C}$ that is independent of the UFEC (3.5). We observe that Ψ is defined for every fast DBRS $(A^{\text{fa}}, B^{\text{fa}}, c_*, \kappa^{\text{fa}})$ and that Ψ only depends on $A^{\text{fa}} - B^{\text{fa}}$ and c_* . The first part of the next result is also shown in [MHM15, Prop. 2.1] or [DLZ18, Lem. 2.3].

Proposition 3.6 (Existence and continuity of interior equilibria). *For a fast DBRS $(A^{\text{fa}}, B^{\text{fa}}, c_*, \kappa^{\text{fa}})$ the energy \mathcal{E} only depends on c_* , and Q_{fa} only depends on $\Gamma_{\text{fa}} = \text{im}(A^{\text{fa}} - B^{\text{fa}})$.*

For each $q \in \mathbf{Q}$, denote by $\Psi(q)$ the unique minimizer of \mathcal{E} on \mathbf{C}_q^{fa} . Then, $\Psi(q)$ is the only equilibrium of $\dot{c} = \mathbf{R}_{\text{fa}}(c)$ that lies in the interior $\mathbf{C}_q^{\text{fa}} \setminus \partial\mathbf{C}_q^{\text{fa}}$. Moreover, the mapping $\Psi : \mathbf{Q} \rightarrow \mathbf{C}$ is continuous, and $\Psi : \text{int } \mathbf{Q} \rightarrow \text{int } \mathbf{C}$ is analytic.

Proof. Step 1. Uniqueness and existence of minimizer: The existence of a global minimizer follows from the coercivity of \mathcal{E} and the closedness of \mathbf{C}_q^{fa} . The uniqueness follows from the convexity of \mathbf{C}_q^{fa} and the strict convexity of \mathcal{E} .

Step 2. Interior property: If \mathbf{C}_q^{fa} is a singleton $\{\hat{c}\}$, then $\Psi(q) = \hat{c}$ automatically lies in the interior. If c^∂ is a point in the boundary and c° a point in the interior of \mathbf{C}_q^{fa} , then there is at least one $k \in I$ such that $c_k^\partial = 0$ and $c_k^\circ > 0$. Since $c_k \mapsto c_k^* \lambda_B(c_k/c_k^*)$ has slope $-\infty$ at $c_k = 0$, we conclude that c^∂ cannot be a minimizer of $\mathcal{E} : c \mapsto \sum_i c_i^* \lambda_B(c_i/c_i^*)$. Hence, $\hat{c} = \Psi(q)$ lies in the interior of \mathbf{C}_q^{fa} .

Step 3. Unique equilibrium property: Since \mathcal{E} is a strict Liapunov function for the RRE, the minimizer $\Psi(q)$ has to be an equilibrium.

For the uniqueness, we consider first the case $\dim(\mathbf{C}_q^{\text{fa}}) = m_{\text{fa}}$, in which case interior points in \mathbf{C}_q^{fa} lie in \mathbf{C}_+ . Hence, for any other equilibrium c_e in the interior of \mathbf{C}_q^{fa} the derivative $D\mathcal{E}(c_e) = (\log(c_i^e/c_i^*))_i$ is well-defined. Moreover, Lemma 2.4 implies $c_e^{\alpha r}/c_e^{*\alpha r} = c_e^{\beta r}/c_e^{*\beta r}$ for all $r \in R_{\text{fa}}$. These two properties yield $D\mathcal{E}(c_e) \cdot \gamma^r = 0$ for $r \in R_{\text{fa}}$. But $D\mathcal{E}(c_e) \in \Gamma_{\text{fa}}^\perp$ and $\mathbf{C}_q^{\text{fa}} \subset c_e + \Gamma_{\text{fa}}$ guarantee that c_e minimizes the convex functional \mathcal{E} on \mathbf{C}_q^{fa} , which yields $c_e = \Psi(q)$.

If $\dim(\mathbf{C}_q^{\text{fa}}) = m(q) < m_{\text{fa}}$ then there exists $I_0 \subset I$ with $m_{\text{fa}} - m(q)$ elements such that $\mathbf{C}_q^{\text{fa}} \subset \{c \in \mathbf{C} \mid c_i = 0 \text{ for all } i \in I_0\}$ and that for interior points $\tilde{c} \in \mathbf{C}_q^{\text{fa}} \setminus \partial\mathbf{C}_q^{\text{fa}}$ we have $\tilde{c}_i > 0$ for $i \notin I_0$. Hence, the above argument can be applied to the reduced system for $\tilde{c} = (c_i)_{i \in I \setminus I_0}$, i.e. the components $c_i = 0, i \in I_0$ are simply ignored.

Step 4. Continuity of Ψ : Consider a sequence $q_k \rightarrow q_\infty$ and let $c_k = \Psi(q_k)$, then we have to show that $c_k \rightarrow c_\infty$. We set $\alpha_k = \mathcal{E}(c_k) = \min \{ \mathcal{E}(c) \mid c \in \mathbf{C}_{q_k}^{\text{fa}} \}$ and choose a subsequence (k_l) such that $\alpha := \liminf_{k \rightarrow \infty} \alpha_k = \lim_{l \rightarrow \infty} \alpha_{k_l}$. By coercivity of \mathcal{E} we know that (c_k) is bounded that there exists a further subsequence (not relabeled) with $c_{k_l} \rightarrow \tilde{c}$ and $Q\tilde{c} = \lim_{l \rightarrow \infty} Qc_{k_l} = \lim_{l \rightarrow \infty} q_{k_l} = q_\infty$. Hence, we obtain the estimate

$$\mathcal{E}(c_\infty) \leq \mathcal{E}(\tilde{c}) = \lim_{l \rightarrow \infty} \mathcal{E}(c_{k_l}) = \lim_{l \rightarrow \infty} \alpha_{k_l} = \alpha. \quad (3.8)$$

Moreover, our given c_∞ and each $\varepsilon > 0$ there exists a $\delta > 0$ such that $Q(B_\varepsilon^{\mathbb{R}^{i^*}}(c_\infty) \cap \mathbf{C})$ contains the set $B_\delta^{\mathbb{R}^{m_{\text{fa}}}}(q_\infty) \cap \mathbf{Q}$. Thus, we find a sequence $(\hat{c}_k)_{k \in \mathbb{N}}$ with $\hat{c}_k \rightarrow c_\infty$ and $Q\hat{c}_k = q_k \rightarrow q_\infty$. Since \mathcal{E} is continuous we conclude

$$\mathcal{E}(c_\infty) = \lim_{k \rightarrow \infty} \mathcal{E}(\hat{c}_k) \geq \liminf_{k \rightarrow \infty} \mathcal{E}(c_k) = \alpha.$$

With (3.8) we conclude $\mathcal{E}(\tilde{c}) = \mathcal{E}(c_\infty)$, which implies $c_k \rightarrow c_\infty = \Psi(q_\infty)$, as desired.

Step 5. Analyticity of Ψ : For $q \in \text{int } \mathbf{Q}$ we have $\Psi(q) \in \mathbf{C}_+ = \text{int } \mathbf{C}$. Hence, $c = \Psi(q)$ can be characterized by the Lagrange principle for constrained minimizers using the Lagrange function $L(c, \lambda) = \mathcal{E}(c) - \mu \cdot (Q_{\text{fa}}c - q)$ with $\mu \in \mathbb{R}^{m_{\text{fa}}}$. This characterization leads to the equation $F(c, \mu) = (0, q)$, where

$$F(c, \mu) := (D\mathcal{E}(c) - Q_{\text{fa}}^\top \mu, Q_{\text{fa}}c).$$

Obviously, $F : \mathbf{C}_+ \times \mathbb{R}^{m_{\text{fa}}} \rightarrow \mathbb{R}^{i^*} \times \mathbb{R}^{m_{\text{fa}}}$ is analytic, and we have $F(\Psi(q), \tilde{\mu}(q)) = (0, q)$ for a suitable $\tilde{\mu}$. If we can show that $DF(\Psi(q), \mu)$ is invertible for all $q \in \text{int } \mathbf{Q}$, then the implicit function theorem implies that the mapping $q \rightarrow (\Psi(q), \tilde{\mu}(q))$ is analytic as well.

The Jacobian of $F(c, \mu)$ is given by $DF(c, \mu) = \begin{pmatrix} D^2\mathcal{E}(c) & -Q_{\text{fa}}^\top \\ Q_{\text{fa}} & 0 \end{pmatrix}$, and we prove that $DF(c, \mu)$ is invertible by showing that its kernel is trivial. Let (w, η) be such that $DF(c, \mu)(w, \eta)^\top = 0$. We conclude that $D^2\mathcal{E}(c)w = Q_{\text{fa}}^\top\eta$ and $Q_{\text{fa}}w = 0$. Since c is positive, the Hessian $D^2\mathcal{E}(c)$ is invertible, and hence, we have $Q_{\text{fa}}D^2\mathcal{E}(c)^{-1}Q_{\text{fa}}^\top\eta = 0$. Multiplying η from the left and using that $D^2\mathcal{E}(c)^{-1}$ is a positive matrix, we have $Q_{\text{fa}}^\top\eta = 0$. Since Q_{fa}^\top is injective, we conclude that $\eta = 0$ which implies that also $w = 0$ due to $D^2\mathcal{E}(c)w = Q_{\text{fa}}^\top\eta = 0$. \square

For later use we observe that by construction we have the relation

$$Q_{\text{fa}}\Psi(q) = q \quad \text{for all } q \in \mathbf{Q}. \quad (3.9)$$

A crucial role in our further analysis will be played by the image of Ψ , which we call the slow manifold:

$$\mathcal{M}_{\text{sl}} := \text{im}(\Psi) = \{ \Psi(q) \mid q \in \mathbf{Q} \} \subset \mathbf{C}, \quad (3.10)$$

which is a closed set that is contained in the set of the fast equilibria \mathcal{E}_{fa} defined in (2.19). The UFEC in (3.5) is made to guarantee that \mathcal{M}_{sl} contains all the fast equilibria:

$$(\text{UFEC}) \iff \mathcal{E}_{\text{fa}} = \mathcal{M}_{\text{sl}}. \quad (3.11)$$

It is important to emphasize that \mathcal{E}_{fa} can be strictly bigger than \mathcal{M}_{sl} , but by Proposition 3.6 these equilibria must be so-called boundary equilibria, i.e. they lie in $\partial\mathbf{C}_{\text{q}}^{\text{fa}} \subset \partial\mathbf{C}$. (In the case that $\mathbf{C}_{\text{q}}^{\text{fa}} \subset \partial\mathbf{C}$ the equilibrium $\Psi(q)$ lies in the boundary of \mathbf{C} , but is not a boundary equilibrium!)

The equilibria on \mathcal{M}_{sl} are stable, since they are global minimizers of the Liapunov function \mathcal{E} in their invariant subset. In contrast, possible boundary equilibria are always unstable, because starting near the equilibrium but in the interior of $\mathbf{C}_{\text{q}}^{\text{fa}}$ gives a solution moving towards $\Psi(q)$, see Figure 3.1. The UFEC may fail if one has autocatalytic reactions where the product $\alpha_i^r\beta_i^r$ is strictly positive for some $i \in I$; see the example treated in Remark 3.9.

The following simple result provides the characterization of the slow manifold \mathcal{M}_{sl} in terms of the potential force $D\mathcal{E}(c)$ and the annihilator of the fast subspace Γ_{fa} .

Lemma 3.7. *Consider a fast DBRS $(A^{\text{fa}}, B^{\text{fa}}, c_*, \kappa^{\text{fa}})$. Then for $c \in \mathbf{C}_+$ we have*

$$D\mathcal{E}(c) \in \Gamma_{\text{fa}}^\perp = \{ \xi \in \mathbb{R}^{i_*} \mid \xi \cdot \gamma^r \text{ for } r \in R_{\text{fa}} \} \iff c \in \mathcal{M}_{\text{sl}}.$$

Proof. Using $D\mathcal{E}(c) = (\log(c_i/c_i^*))_{i \in I}$ we find, for all $r \in R_{\text{fa}}$,

$$0 = D\mathcal{E}(c) \cdot \gamma^r = \log\left(\frac{c^{\alpha^r}}{c_*^{\alpha^r}} \frac{c_*^{\beta^r}}{c^{\beta^r}}\right) \iff \frac{c^{\alpha^r}}{c_*^{\alpha^r}} = \frac{c^{\beta^r}}{c_*^{\beta^r}}$$

With Proposition 3.6 and the definition of \mathcal{M}_{sl} in (3.10) we obtain the desired result. \square

Finally, we show that the UFEC is invariant under tilting. This is a nice consequence of the fact that tilting in systems satisfying the DBC allows us easily to follow the changes in the set \mathcal{E}_{fa} of fast equilibria.

Corollary 3.8 (UFEC and tilting). *Consider a fast DBRS $(A^{\text{fa}}, B^{\text{fa}}, c_*, \kappa^{\text{fa}})$ and general tilt vectors $\eta \in \mathbb{R}^{i_*}$. Denote by $\mathcal{E}_{\text{fa}}^\eta$ and $\mathcal{M}_{\text{sl}}^\eta$ the set of equilibria and the slow manifold, respectively, for the fast DBRS $(A^{\text{fa}}, B^{\text{fa}}, \mathbb{D}^\eta c_*, \kappa^{\text{fa}})$. Then, the following holds:*

(a) $\mathcal{E}_{\text{fa}}^\eta = \mathbb{D}^\eta \mathcal{E}_{\text{fa}}^0$ and $\mathcal{M}_{\text{sl}}^\eta = \mathbb{D}^\eta \mathcal{M}_{\text{sl}}^0$,

(b) $(A^{\text{fa}}, B^{\text{fa}}, c_*, \kappa^{\text{fa}})$ satisfies UFEC if and only if $(A^{\text{fa}}, B^{\text{fa}}, \mathbb{D}^\eta c_*, \kappa^{\text{fa}})$ does so.

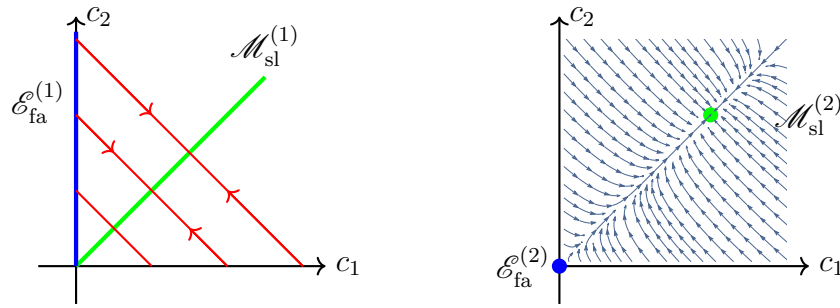


Figure 3.1: The slow manifolds $\mathcal{M}_{\text{sl}}^{(k)}$ (green) are strictly contained in $\mathcal{E}_{\text{fa}}^{(k)}$ (blue and green). The blue points are unstable, while the green points are stable. In the case (1) the invariant sets \mathbf{C}_q^{fa} (red) are one-dimensional, while in case (2) we have $\mathbf{C}_0^{\text{fa}} = \mathbf{C}$.

Proof. By Lemma 2.4 the equilibria $c \in \mathcal{E}_{\text{fa}}^0$ are given by the condition $\frac{c^{\alpha r}}{c_*^{\alpha r}} = \frac{c^{\beta r}}{c_*^{\beta r}}$ for all $r \in R_{\text{fa}}$. However, changing c and c_* into $\mathbb{D}^\eta c$ and $\mathbb{D}^\eta c_*$, respectively, shows that the condition remains the same.

Moreover, for $c \in \mathbf{C}_+$ we have $\text{D}\mathcal{E}^\eta(\mathbb{D}^\eta c) = \text{D}\mathcal{E}(c)$ by construction. Since $c \in \mathbf{C}_+ \cap \mathcal{M}_{\text{sl}}^0$ is equivalent to $\text{D}\mathcal{E}(c) \in \Gamma_{\text{fa}}^\perp$ we have $\mathbb{D}^\eta c \in \mathcal{M}_{\text{sl}}^\eta$. By the continuity of $\Psi = \Psi^0$ and Ψ^η (see Proposition 3.6) we conclude $\mathbb{D}^\eta \mathcal{M}_{\text{sl}}^0 \subset \mathcal{M}_{\text{sl}}^\eta$. As \mathbb{D}^η is invertible, we can revert the argument and arrive at $\mathbb{D}^\eta \mathcal{M}_{\text{sl}}^0 = \mathcal{M}_{\text{sl}}^\eta$. Thus, (a) is established.

With (a) we see that $\mathcal{E}_{\text{fa}}^0 = \mathcal{M}_{\text{sl}}^0$ is equivalent to $\mathcal{E}_{\text{fa}}^\eta = \mathcal{M}_{\text{sl}}^\eta$, and (b) is established as well. \square

3.4 Examples and problems without the UFEC

In the following two remarks, we firstly provide a few examples where UFEC does not hold and secondly show that our main result in Theorem 3.4 fails without UFEC.

Remark 3.9 (Examples without UFEC). The simplest example of a RRE not satisfying the UFEC condition is the autocatalytic reaction $2X \rightleftharpoons X$, leading to the RRE $\dot{c} = \frac{1}{\varepsilon}(c - c^2)$, where $\Gamma = \Gamma_{\text{fa}} = \mathbb{R}$ and $m = m_{\text{fa}} = 0$. In particular, the fast stoichiometric subset $\mathbf{C} = \mathbf{C}_0^{\text{fa}} = [0, \infty[$ contains the interior equilibrium $c_* = 1$ and the boundary equilibrium $c = 0$.

Next, we consider two different fast systems for two species, the first with the single autocatalytic reaction $X_1 + X_2 \rightleftharpoons 2X_1$ and the second with two non-autocatalytic reactions $2X_1 \rightleftharpoons X_2$ and $X_1 \rightleftharpoons 2X_2$. The fast RREs read

$$c' = \mathbf{R}^{(1)}(c) = (c_1^2 - c_1 c_2) \begin{pmatrix} -1 \\ 1 \end{pmatrix}, \quad c' = \mathbf{R}^{(2)}(c) = (c_1^2 - c_2) \begin{pmatrix} -2 \\ 1 \end{pmatrix} + (c_1 - c_2^2) \begin{pmatrix} -1 \\ 2 \end{pmatrix}.$$

The conserved quantities are given by the matrices

$$Q_{\text{fa}}^{(1)} c = c_1 + c_2 \in \mathbf{Q}^{(1)} = [0, \infty[\quad \text{and} \quad Q_{\text{fa}}^{(2)} c = 0 \in \mathbf{Q}^{(2)} = \{0\}.$$

The functions Ψ for the minimizers of \mathcal{E} over \mathbf{C}_q^{fa} are given by $\Psi^{(1)}(q) = (q/2, q/2)^\top$ and $\Psi^{(2)}(0) = (1, 1)^\top$ leading to

$$\mathcal{M}_{\text{sl}}^{(1)} = \{(z, z)^\top \mid z \geq 0\} \quad \text{and} \quad \mathcal{M}_{\text{sl}}^{(2)} = \{(1, 1)^\top\}.$$

However, the set of fast equilibria is bigger in both cases:

$$\mathcal{E}_{\text{fa}}^{(1)} = \mathcal{M}_{\text{sl}}^{(1)} \dot{\cup} \{(0, z)^\top \mid z \geq 0\} \quad \text{and} \quad \mathcal{E}_{\text{fa}}^{(2)} = \mathcal{M}_{\text{sl}}^{(2)} \dot{\cup} \{(0, 0)^\top\}.$$

Figure 3.1 displays the invariant sets \mathbf{C}_q^{fa} , \mathcal{M}_{sl} , and \mathcal{E}_{fa} for both cases.

To the knowledge of the authors there are currently no general sufficient conditions on the fast DBRS $(A^{\text{fa}}, B^{\text{fa}}, c_*, \kappa^{\text{fa}})$ available that guarantee the validity of the UFEC. However, in many applications the number $\#(R_{\text{fa}})$ of fast reactions is rather small such that an analysis of the fast RRE is easily done.

The next remark shows that Theorem 3.4 does not hold if the UFEC in (3.5) does not hold.

Remark 3.10 (A counterexample with jumps). We return to the first RRE $\dot{c} = \frac{1}{\varepsilon}(c - c^2)$ of the previous remark. The associated dissipation potential and slope functions are

$$\mathcal{R}_\varepsilon^*(c, \xi) = \frac{c^{3/2}}{\varepsilon} \mathbf{C}^*(\xi) \quad \text{and} \quad \mathcal{S}_\varepsilon(c) = \frac{2}{\varepsilon} c (c^{1/2} - 1)^2.$$

Moreover, the dissipation functional \mathfrak{D}_ε takes the form

$$\mathfrak{D}_\varepsilon(c) = \int_0^T \left\{ \frac{c^{3/2}}{\varepsilon} \mathbf{C} \left(\frac{\varepsilon \dot{c}}{c^{3/2}} \right) + \frac{2c}{\varepsilon} (c^{1/2} - 1)^2 \right\} dt.$$

Note that $c \equiv 0$ and $c \equiv 1$ yield $\mathfrak{D}_\varepsilon(c) = 0$. Moreover, fixing $t_* \in]0, T[$ the trajectories $\tilde{c}^\varepsilon(t) = e^{(t-t_*)/\varepsilon} / (1 + e^{(t-t_*)/\varepsilon})$ are exact solutions of the RRE $\dot{c} = \frac{1}{\varepsilon}(c - c^2)$, hence the energy-dissipation principle gives $\mathfrak{D}_\varepsilon(\tilde{c}^\varepsilon) = \mathcal{E}(\tilde{c}^\varepsilon(0)) - \mathcal{E}(\tilde{c}^\varepsilon(T)) \leq \mathcal{E}(0) - \mathcal{E}(1) = 1$. Thus, the limit function \tilde{c}^0 with $\tilde{c}^0(t) = 0$ for $t < t_*$ and $\tilde{c}^0(t) = 1$ for $t > t_*$ is not continuous but must satisfy $\mathfrak{D}_0(\tilde{c}^0) \leq 1$, which is in contradiction to Theorem 3.4.

Indeed, using the Modica-Mortola approach as described in [Bra02, Sec. 6] (involving the estimate $\mathcal{R}_\varepsilon(c, \dot{c}) + \mathcal{R}_\varepsilon^*(c, -D\mathcal{E}(c)) \geq -D\mathcal{E}(c)\dot{c}$) it can be shown that $\mathfrak{D}_\varepsilon \xrightarrow{\Gamma} \mathfrak{D}_0$ in $L^1([0, T]; \mathbb{R})$, where \mathfrak{D}_0 is finite only on piecewise constant functions taking values in $\{0, 1\}$ only. Moreover, for these functions $\mathfrak{D}_0(c)$ equals the number of jumps times $\mathcal{E}(0) - \mathcal{E}(1) = 1$. The same was also observed in [Ste19].

4 The effective GS and the limiting equation

Here we present two different ways to derive the the limiting equation from our effective gradient system. The first one is in line with the coarse-graining approach developed in [MiS19], where a lower-dimensional system is derived for the coarse-grained variable $q = Q_{\text{fa}}c$ and the restriction $c = \Psi(q)$ is built into the model. The second one follows [Bot03] and [DLZ18, Thm. 4.5], where the variable c is maintained and the constraint $c \in \mathcal{M}_{\text{sl}}$ is realized by a suitable projection.

In both cases we start from the Γ -limit \mathfrak{D}_0 of the dissipation functionals \mathfrak{D}_ε . Using the energy-dissipation principle from Theorem 2.1 the limiting evolution can be recovered from

$$\mathcal{E}(c(T)) + \mathfrak{D}_0(c; 0, T) \leq \mathcal{E}(c(0)), \quad \mathfrak{D}(c; 0, T) = \int_0^T \{ \mathcal{R}_{\text{eff}}(c, \dot{c}) + \mathcal{R}_{\text{eff}}^*(c, -D\mathcal{E}(c)) \} dt \quad (4.1)$$

via the chain rule, which holds in the finite-dimensional space $\mathbf{C} \subset \mathbb{R}^{i^*}$.

Any solution satisfies the condition

$$\int_0^T \mathcal{S}_0(c(t)) dt \leq \mathfrak{D}_0(c; 0, T) = \int_0^T \{ \mathcal{R}_{\text{eff}}(c, \dot{c}) + \mathcal{R}_{\text{eff}}^*(c, -D\mathcal{E}(c)) \} dt \leq \mathcal{E}(c(0)) - \mathcal{E}(c(T)) < \infty,$$

where by the UFEC the function \mathcal{S}_0 assumes the value $+\infty$ for $c \notin \mathcal{M}_{\text{sl}}$. Hence, the continuity of c implies that $c(t) \in \mathcal{M}_{\text{sl}}$ for all $t \in [0, T]$. Thus, setting $\mathbf{q}(t) := Q_{\text{fa}}c(t)$ and using the relation (3.9) we have $c(t) = \Psi(\mathbf{q}(t))$ for all $t \in [0, T]$. We recall that the properties

$$c \in C^0([0, T]; \mathbf{C}) \quad \text{and} \quad \mathbf{q} = Q_{\text{fa}}c \in W^{1,1}([0, T]; \mathbb{R}^{m_{\text{fa}}})$$

are consequences of Theorem 3.4.

4.1 Coarse-graining approach

In this part we concentrate solely on the slow variables \mathbf{q} and define

$$E(\mathbf{q}) := \mathcal{E}(\Psi(\mathbf{q})) \quad \text{and} \quad R^*(\mathbf{q}, \zeta) := \mathcal{R}_{\text{sl}}^*(\Psi(\mathbf{q}), Q_{\text{fa}}^\top \zeta), \quad (4.2)$$

which defines a reduced gradient system (\mathbf{Q}, E, R) for the coarse-grained state $\mathbf{q} \in \mathbf{Q} \subset \mathbb{R}^{m_{\text{fa}}}$. In particular, $R^* : \mathbf{Q} \times \mathbb{R}^{m_{\text{fa}}} \rightarrow [0, \infty]$ is a well-defined dual dissipation potential as $Q_{\text{fa}}^\top : \mathbb{R}^{m_{\text{fa}}} \rightarrow \mathbb{R}^{i_*}$.

The main result of this subsection will be that the gradient-flow equation for the reduced gradient system (\mathbf{Q}, E, R) is indeed the limiting equation and it has a simple representation in terms of \mathbf{R}_{sl} , Q_{fa} , and Ψ :

$$\dot{\mathbf{q}} = \partial_\zeta R^*(\mathbf{q}, -DE(\mathbf{q})) = Q_{\text{fa}} \mathbf{R}_{\text{sl}}(\Psi(\mathbf{q})). \quad (4.3)$$

Thus, (\mathbf{Q}, E, R) provides an exact nonlinear coarse-graining in the sense of [MaM20, Sec. 6.1], where the relation $I_{m_{\text{fa}}} = Q_{\text{fa}} D\Psi(\mathbf{q})$ simplifies the formula for R^* compared to [MaM20, Eq. (6.2)].

Remark 4.1. This theory is a nonlinear generalization of the coarse-graining theory developed in [MiS19], where $\hat{c} = MA_{\text{sl}}N\hat{c}$ is the coarse-grained equation. In our case the role of the reconstruction operator $N : \mathbb{R}^J \rightarrow \mathbb{R}^I$ is played by the nonlinear mapping $\Psi : \mathbf{Q} \rightarrow \mathbf{C}$, while the role of the coarse-graining operator $M : \mathbb{R}^I \rightarrow \mathbb{R}^J$ is our linear operator $Q_{\text{fa}} : \mathbf{C} \rightarrow \mathbf{Q}$.

The following result provides first the justification of the second identity in (4.3), and then shows that this equation is indeed the limiting equation obtained from the energy-dissipation principle for \mathcal{E} and \mathcal{D}_0 .

Proposition 4.2 (Reduced gradient structure). *Let the DBRS $(A, B, c_*, \hat{k}^\varepsilon)$ be given as in Section 2.4 and satisfy the UFEC (3.5), and let (\mathbf{Q}, E, R^*) be defined as above. Then the following identities are valid:*

(a) For $\mathbf{q} \in \text{int } \mathbf{Q}$ we have

$$Q_{\text{fa}} D\Psi(\mathbf{q}) = I_{m_{\text{fa}}}, \quad \text{and}, \quad Q_{\text{fa}}^\top D\Psi(\mathbf{q})^\top \text{ is a projection onto } \text{im}(Q_{\text{fa}}^\top) = \Gamma_{\text{fa}}^\perp \quad (4.4)$$

(b) For $\mathbf{q} \in \text{int } \mathbf{Q}$ we have $\partial_\zeta R^*(\mathbf{q}, -DE(\mathbf{q})) = Q_{\text{fa}} \mathbf{R}_{\text{sl}}(\Psi(\mathbf{q}))$;

(c) the primal dissipation potential R takes the form

$$R(\mathbf{q}, w) = \inf \{ \mathcal{R}_{\text{sl}}(\Psi(\mathbf{q}), v) \mid Q_{\text{fa}} v = w \} = \mathcal{R}_{\text{eff}}(\Psi(\mathbf{q}), \tilde{v}) \text{ whenever } Q_{\text{fa}} \tilde{v} = w;$$

(d) For $\mathbf{q} \in \text{int } \mathbf{Q}$ we have $R^*(\mathbf{q}, -DE(\mathbf{q})) = \mathcal{S}_{\text{sl}}(\Psi(\mathbf{q})) =: S(\mathbf{q})$;

(e) $\mathcal{D}_0(\Psi(\mathbf{q})) = \int_0^T \{ R(\mathbf{q}, \dot{\mathbf{q}}) + S(\mathbf{q}) \} dt$.

In part (e) it is crucial to observe that for differentiable $t \mapsto \mathbf{q}(t)$ we cannot guarantee that $t \mapsto c(t) = \Psi(\mathbf{q}(t))$ is differentiable as well, since $\mathbf{q}(t)$ need not remain in the interior of \mathbf{Q} . However, for \mathfrak{D}_0 we only need continuity of c and the differentiability of $t \mapsto Q_{\text{fa}}c(t) = \dot{\mathbf{q}}(t)$, where we used $\mathbf{q} = Q_{\text{fa}}\Psi(\mathbf{q})$, see (3.9).

Proof. For part (a), we use that Ψ is differentiable in $\text{int } \mathbf{Q}$. Differentiating the relation $Q_{\text{fa}}\Psi(\mathbf{q}) = \mathbf{q}$ yields $Q_{\text{fa}}D\Psi(\mathbf{q}) = I_{m_{\text{fa}}}$. In particular, this implies that $D\Psi(\mathbf{q})Q_{\text{fa}}$ is a projection, and hence also its transpose $Q_{\text{fa}}^\top D\Psi(\mathbf{q})^\top$.

To show part (b) we first use the chain rule $DE(\mathbf{q}) = D\Psi(\mathbf{q})^\top D\mathcal{E}(\Psi(\mathbf{q}))$. With Lemma 3.7 and part (a) we have that $D\mathcal{E}(\Psi(\mathbf{q})) = Q_{\text{fa}}^\top D\Psi(\mathbf{q})^\top D\mathcal{E}(\Psi(\mathbf{q}))$, which yields

$$\begin{aligned} \partial_\zeta R^*(\mathbf{q}, -DE(\mathbf{q})) &= Q_{\text{fa}}^\top D_\xi \mathcal{R}_{\text{sl}}^*(\Psi(\mathbf{q}), -Q_{\text{fa}}^\top D\Psi(\mathbf{q})^\top D\mathcal{E}(\Psi(\mathbf{q}))) \\ &= Q_{\text{fa}}^\top D_\xi \mathcal{R}_{\text{sl}}^*(\Psi(\mathbf{q}), -D\mathcal{E}(\Psi(\mathbf{q}))) = Q_{\text{fa}} \mathbf{R}_{\text{sl}}(\Psi(\mathbf{q})). \end{aligned}$$

For (c) we establish the relation $R^* = \mathcal{L}R$ via the Legendre transformation \mathcal{L} :

$$\begin{aligned} (\mathcal{L}R(q, \cdot))(\zeta) &= \sup \{ \zeta \cdot w - R(\mathbf{q}, w) \mid w \in \mathbb{R}^{m_{\text{fa}}} \} \\ &= \sup \left\{ \zeta \cdot w + \sup \{ -\mathcal{R}_{\text{sl}}(\Psi(\mathbf{q}), v) \mid Q_{\text{fa}}v = w \} \mid w \in \mathbb{R}^{m_{\text{fa}}} \right\} \\ &= \sup \{ \zeta \cdot w - \mathcal{R}_{\text{sl}}(\Psi(\mathbf{q}), v) \mid Q_{\text{fa}}v = w \} \\ &= \sup \{ \zeta \cdot Q_{\text{fa}}v - \mathcal{R}_{\text{sl}}(\Psi(\mathbf{q}), v) \mid v \in \mathbb{R}^{i^*} \} = \mathcal{R}_{\text{sl}}^*(\Psi(\mathbf{q}), Q_{\text{fa}}^\top \zeta) = R^*(\mathbf{q}, \zeta). \end{aligned}$$

Part (d) follows similarly as part (b) by inserting $DE(\mathbf{q}) = D\Psi(\mathbf{q})^\top D\mathcal{E}(\Psi(\mathbf{q}))$ and $D\mathcal{E}(\Psi(\mathbf{q})) = Q_{\text{fa}}^\top D\Psi(\mathbf{q})^\top D\mathcal{E}(\Psi(\mathbf{q}))$ into the definition of R^* via $\mathcal{R}_{\text{sl}}^*$.

For part (e) we first observe that $\mathcal{S}_{\text{sl}}(\Psi(\mathbf{q})) = S(\mathbf{q})$ for all $\mathbf{q} \in \mathbf{Q}$ by definition. For the rate part $\mathcal{R}_{\text{eff}}(c, \dot{c})$ part (c) established that the dependence on \dot{c} is only through $Q_{\text{fa}}\dot{c}$. But relation (3.9) gives $\frac{d}{dt}Q_{\text{fa}}\Psi(\mathbf{q}(t)) = \dot{\mathbf{q}}(t)$, and the relation $\mathcal{R}_{\text{eff}}(c, \dot{c}) = \mathcal{R}_{\text{eff}}(\Psi(\mathbf{q}), D\Psi(\mathbf{q})\dot{\mathbf{q}}) = R(\mathbf{q}, \dot{\mathbf{q}})$ holds even $\mathbf{q}(t)$ touching the boundary of \mathbf{Q} . \square

The next result shows that the reduced gradient-flow equation (4.3) indeed is the limiting equation for the fast-slow RRE (2.14) in the sense that for solutions $c^\varepsilon : [0, T] \rightarrow \mathbf{C}$ any accumulation point $\mathbf{q} : [0, T] \rightarrow \mathbf{Q}$ of the family $(Q_{\text{fa}}c^\varepsilon)$ solves indeed (4.3). The assumptions on the initial conditions $c^\varepsilon(0)$ are special to avoid a potential jump at $t = 0$, see Section 2.4. The proof is based on the energy-dissipation principle and follows [Mie16, Thm. 3.3.3] or [MMP19, Lem. 2.8] with some special care because of the degeneracies and singularities of the limiting problem.

Proposition 4.3 (Reduced limiting equation). *Consider a fast-slow DBRS $(A, B, c_*, \widehat{\kappa}^\varepsilon)$ satisfying the UFEC (3.5) and let $c^\varepsilon : [0, T] \rightarrow \mathbb{R}^{i^*}$ be a family of solutions of the fast-slow RRE (2.14). If along a subsequence (not relabeled) we have $c^\varepsilon \rightarrow c^0$ in $L^1([0, T]; \mathbf{C})$ and $c^\varepsilon(0) \rightarrow \bar{c}_0 \in \mathcal{M}_{\text{sl}}$, then $Q_{\text{fa}}c^\varepsilon \rightarrow \mathbf{q} := Q_{\text{fa}}c^0$ weakly in $W^{1,1}([0, T]; \mathbf{Q})$ and strongly in $C^0([0, T]; \mathbf{Q})$, and \mathbf{q} solves the reduced gradient-flow equation (4.3) with initial condition $\mathbf{q}(0) = Q_{\text{fa}}\bar{c}_0$.*

Proof. The solutions c^ε satisfy the EDB $\mathcal{E}(c^\varepsilon(T)) + \mathfrak{D}_\varepsilon(c^\varepsilon) = \mathcal{E}(c^\varepsilon(0))$. Using that $c^\varepsilon \rightarrow c^0$ in $L^1([0, T]; \mathbb{R}^{i^*})$ and $\limsup_{\varepsilon \rightarrow 0^+} \mathfrak{D}_\varepsilon(c^\varepsilon) \leq \lim_{\varepsilon \rightarrow 0^+} \mathcal{E}(c^\varepsilon(0)) = \mathcal{E}(\bar{c}_0) < \infty$, we obtain $\mathbf{q}^\varepsilon := Q_{\text{fa}}c^\varepsilon \rightarrow \mathbf{q}$ weakly in $W^{1,1}([0, T]; \mathbf{Q})$ and strongly in $C^0([0, T]; \mathbf{Q})$ by invoking Theorem 5.1(ii). Moreover, because of $\bar{c}_0 \in \mathcal{M}_{\text{sl}}$ and $\mathbf{q}^\varepsilon(0) = Q_{\text{fa}}c^\varepsilon(0) \rightarrow Q_{\text{fa}}\bar{c}_0$ we have $\mathbf{q}(0) = Q_{\text{fa}}\bar{c}_0$ and

hence $\bar{c}_0 = \Psi(q(0))$ and $\mathcal{E}(\bar{c}_0) = \mathcal{E}(q(0))$. Passing to the limit $\varepsilon \rightarrow 0^+$ using the liminf estimate in $\mathfrak{D}_\varepsilon \xrightarrow{\Gamma_{\mathbb{E}}} \mathfrak{D}_0$ we arrive at

$$\mathcal{E}(q(T)) + \mathfrak{D}_0(\Psi(q)) \leq \mathcal{E}(c^0(T)) + \mathfrak{D}_0(c^0) \leq \mathcal{E}(\bar{c}_0) = \mathcal{E}(q(0)).$$

Because $\mathfrak{D}_0(\Psi(\cdot))$ has the $\mathbb{R} \oplus \mathbb{R}^*$ structure (cf. Proposition 4.2(d+e)) the energy-dissipation principle shows that q solves the reduced RRE (4.3). \square

4.2 The projection approach

By contrast to Section 4.1 above, in this section we maintain the variable c . First, we justify the limiting equation (2.20) with the constraint $c \in \mathcal{M}_{\text{sl}}$ and the Lagrange multiplier $\lambda(t) \in \Gamma_{\text{fa}}$. Secondly, we show that for positive solutions the evolution can be written as an ODE involving a suitable projection. Finally, we compare this to the reduced limiting equation (4.3).

Proposition 4.4 (Limiting equation with constraint). *For a fast-slow DBRS $(A, B, c_*, \widehat{\kappa}^\varepsilon)$ satisfying the UFEC (3.5) we consider a family $c^\varepsilon : [0, T] \rightarrow \mathbb{R}^{i_*}$ of solutions of the fast-slow RRE (2.14). If along a subsequence (not relabeled) we have $c^\varepsilon \rightarrow c^0$ in $L^1([0, T]; \mathbf{C})$ and $c^\varepsilon(0) \rightarrow \bar{c}_0 \in \mathcal{M}_{\text{sl}}$, then there exists $c \in C^0([0, T]; \mathbf{C})$ such that $c(t) = c^0(t)$ a.e. in $[0, T]$, $c(0) = \bar{c}_0$, $Q_{\text{fa}}c \in W^{1,1}([0, T]; \mathbf{Q})$, and c solves the limiting equation with constraint:*

$$\dot{c}(t) = \mathbf{R}_{\text{sl}}(c(t)) + \lambda(t), \quad \lambda(t) \in \Gamma_{\text{fa}}, \quad c(t) \in \mathcal{M}_{\text{sl}}. \quad (4.5)$$

Proof. We proceed as in the proof of Proposition 4.3 but stay with c rather than reducing to $q = Q_{\text{fa}}c$. The solutions c^ε satisfy the EDB $\mathcal{E}(c^\varepsilon(T)) + \mathfrak{D}_\varepsilon(c^\varepsilon) = \mathcal{E}(c^\varepsilon(0))$. Using $c^\varepsilon \rightarrow c^0$ in $L^1([0, T]; \mathbb{R}^{i_*})$ and $\limsup_{\varepsilon \rightarrow 0^+} \mathfrak{D}_\varepsilon(c^\varepsilon) \leq \lim_{\varepsilon \rightarrow 0^+} \mathcal{E}(c^\varepsilon(0)) = \mathcal{E}(\bar{c}_0) < \infty$, we have $Q_{\text{fa}}c^\varepsilon \rightarrow q$ weakly in $W^{1,1}([0, T]; \mathbf{C})$ and strongly in $C^0([0, T]; \mathbb{R}^{i_*})$, see Theorem 5.1(ii). With this we define $c(t) = \Psi(q(t))$ for $t \in [0, T]$ such that $c \in C^0([0, T]; \mathbf{C})$ and $Q_{\text{fa}}c(t) = q(t)$.

Passing to the limit $\varepsilon \rightarrow 0^+$ in the EDB we obtain $\mathcal{E}(c(T)) + \mathfrak{D}_0(c) \leq \mathcal{E}(c(0))$, and the energy-dissipation principle gives the gradient-flow equation

$$\dot{c} \in \partial_\xi \mathcal{R}_{\text{eff}}^*(c, -D\mathcal{E}(c)) = \partial_\xi \left(\mathcal{R}_{\text{sl}}^*(c, -D\mathcal{E}(c)) + \chi_{\Gamma_{\text{fa}}^\perp}(-D\mathcal{E}(c)) \right). \quad (4.6)$$

For a linear subspace $Y \subset \mathbb{R}^{i_*}$ the set-valued convex subdifferential $\partial \chi_{Y^\perp}(\xi)$ equals Y for $\xi \in Y^\perp$ and \emptyset otherwise, hence the last relation has the form

$$\dot{c} \in \partial_\xi \mathcal{R}_{\text{sl}}^*(c, -D\mathcal{E}(c)) + \Gamma_{\text{fa}} = \mathbf{R}_{\text{sl}}(c) + \Gamma_{\text{fa}} \quad \text{and} \quad D\mathcal{E}(c) \in \Gamma_{\text{fa}}^\perp.$$

With Lemma 3.7 we can replace the last constraint by $c \in \mathcal{M}_{\text{sl}}$, and (4.5) is established. \square

To obtain an ODE of the form $\dot{c} = V(c)$ instead of the limiting equation (4.5) with constraint, we have to resolve the constraint $D\mathcal{E}(c) \in \Gamma_{\text{fa}}^\perp$. For any curve $s \rightarrow \tilde{c}(s) \in \mathcal{M}_{\text{sl}} \cap \mathbf{C}_+$ we have $D\mathcal{E}(\tilde{c}(s)) \in \Gamma_{\text{fa}}^\perp$ and taking the derivative with respect to s , we find

$$\dot{\tilde{c}}(s) \in T_{\tilde{c}(s)} \mathcal{M}_{\text{sl}} \quad \text{and} \quad D^2\mathcal{E}(\tilde{c}(s))\dot{\tilde{c}}(s) \in \Gamma_{\text{fa}}^\perp.$$

Hence, for $c \in \mathcal{M}_{\text{sl}} \cap \mathbf{C}_+$ the tangent space $T_c \mathcal{M}_{\text{sl}}$ of \mathcal{M}_{sl} at c is given by

$$T_c \mathcal{M}_{\text{sl}} = (\mathbb{H}(c))^{-1} \Gamma_{\text{fa}}^\perp \quad \text{with} \quad \mathbb{H}(c) := D^2\mathcal{E}(c) = \text{diag}(1/c_1, \dots, 1/c_{i_*}).$$

With this we obtain the following representation of the limiting equation, which matches that in [Bot03, Thm. 2(b)] and [DLZ18, Thm. 4.5]. Our result is more general, since we do not need to assume that the stoichiometric vectors $\{\gamma^r \mid r \in R_{\text{fa}}\}$ are linearly independent.

Proposition 4.5 (Limiting equation for $c \in \mathbf{C}_+$). *A curve $c : [0, T] \rightarrow \mathbf{C}_+$ is a solution (4.5) if and only if*

$$\dot{c} = (I - \mathbb{P}(c)) \mathbf{R}_{\text{sl}}(c) \quad \text{and} \quad c(0) \in \mathcal{M}_{\text{sl}}. \quad (4.7)$$

where the projector $\mathbb{P}(c) \in \mathbb{R}^{i_* \times i_*}$ is defined via $\text{im } \mathbb{P}(c) = \Gamma_{\text{fa}}$ and $\ker \mathbb{P}(c) = \mathbb{H}(c)^{-1} \Gamma_{\text{fa}}^\perp$.

Proof. Step 1. Definition of the projector $\mathbb{P}(c)$: The projector is uniquely defined if $Y_{\text{R}} := \Gamma_{\text{fa}}$ and $Y_{\text{K}} := \mathbb{H}(c)^{-1} \Gamma_{\text{fa}}^\perp$ provide a direct decomposition of \mathbb{R}^{i_*} . Assuming $v \in Y_{\text{R}} \cap Y_{\text{K}}$ we have $v \in \Gamma_{\text{fa}}$ and $\mathbb{H}(c)v \in \Gamma_{\text{fa}}^\perp$. This implies $v \cdot \mathbb{H}(c)v = 0$, but since $\mathbb{H}(c)$ is positive definite we arrive at $v = 0$. Hence, $Y_{\text{R}} \cap Y_{\text{K}} = \{0\}$. Obviously, $\dim Y_{\text{R}} + \dim Y_{\text{K}} = i_*$, so that $\mathbb{R}^{i_*} = Y_{\text{R}} \oplus Y_{\text{K}}$ is established.

Step 2. (4.7) \implies (4.5): We set $\lambda(t) = -\mathbb{P}(c(t)) \mathbf{R}_{\text{sl}}(c)$, and with (4.7) we obtain

$$\dot{c}(t) = \mathbf{R}_{\text{sl}}(c(t)) - \mathbb{P}(c(t)) \mathbf{R}_{\text{sl}}(c(t)) = \mathbf{R}_{\text{sl}}(c(t)) + \lambda(t) \quad \text{with } \lambda(t) \in \Gamma_{\text{fa}}.$$

Moreover, $\mathbb{P}(c(t)) \dot{c}(t) = \mathbb{P}(c(t)) (I - \mathbb{P}(c(t))) \mathbf{R}_{\text{sl}}(c) = 0$, which implies $\dot{c} \in \mathbb{H}(c)^{-1} \Gamma_{\text{fa}}^\perp = \mathbb{T}_{c(t)} \mathcal{M}_{\text{sl}}$. Hence, with $c(0) \in \mathcal{M}_{\text{sl}}$ we obtain $c(t) \in \mathcal{M}_{\text{sl}}$ for all $t \in [0, T]$, and (4.5) is established.

Step 3. (4.5) \implies (4.7): From $c(t) \in \mathcal{M}_{\text{sl}}$ we obtain $\dot{c}(t) \in \mathbb{T}_{c(t)} \mathcal{M}_{\text{sl}} = \mathbb{H}(c(t))^{-1} \Gamma_{\text{fa}}^\perp$ and conclude $0 = \mathbb{P}(c) \dot{c} = \mathbb{P}(c) \mathbf{R}_{\text{sl}}(c) + \mathbb{P}(c) \lambda$. Using $\lambda \in \text{im } \mathbb{P}(c) = \Gamma_{\text{fa}}$ we have $\mathbb{P}(c) \lambda = \lambda$ and find

$$(I - \mathbb{P}(c)) \mathbf{R}_{\text{sl}}(c) = \mathbf{R}_{\text{sl}}(c) - \mathbb{P}(c) \mathbf{R}_{\text{sl}}(c) = \mathbf{R}_{\text{sl}}(c) + \mathbb{P}(c) \lambda = \mathbf{R}_{\text{sl}}(c) + \lambda = \dot{c},$$

which is the desired equation (4.7). □

To compare the last result with the reduced limiting equation (4.3), we simply use the relation $c(t) = \Psi(q(t))$ and the fact that Ψ is smooth on $\text{int } \mathbf{Q}$. From this we obtain

$$(I - \mathbb{P}(c)) \mathbf{R}_{\text{sl}}(c) = \dot{c} = D\Psi(q) \dot{q} = D\Psi(q(t)) Q_{\text{fa}} \mathbf{R}_{\text{sl}}(\Psi(q)) = D\Psi(q(t)) Q_{\text{fa}} \mathbf{R}_{\text{sl}}(c).$$

Thus, we can conclude that for $c = \Psi(q) \in \mathcal{M}_{\text{sl}}$ we have the identity

$$(I - \mathbb{P}(c)) = D\Psi(q) Q_{\text{fa}},$$

since the above identity must hold for all possible right-hand sides \mathbf{R}_{sl} . This can also be shown by using the identity $c = \Psi(Q_{\text{fa}} c)$ for all $c \in \mathcal{M}_{\text{sl}}$ and taking derivatives in the direction $v \in \Gamma_{\text{fa}}$ and $w \in \mathbb{T}_c \mathcal{M}_{\text{sl}}$, respectively. In particular, this provides the explicit form of the projection of Proposition 4.2(a).

4.3 An example for the effective gradient system

In the following example we consider a system with $i_* = 5$ species and $r_* = 2$ bimolecular reactions, one fast and one slow. As a result we obtain a limiting equation with one reaction that is no longer of mass-action type but involves all species. Taking a further EDP limit (done only formally) we recover a trimolecular reaction of mass-action type again.

We consider the following two reactions



which give rise to the two stoichiometric vectors

$$\gamma^{\text{fa}} = (1, 1, -1, 0, 0)^\top \quad \text{and} \quad \gamma^{\text{sl}} = (0, 0, 1, 1, -1)^\top.$$

Assuming the steady state $c_* = (1, 1, \varrho, 1, 1)^\top$ and the reaction coefficients $\widehat{\kappa}^\varepsilon = (\kappa^{\text{fa}}/\varepsilon, \kappa^{\text{sl}})$ the RRE (2.14) takes the form

$$\dot{c} = -\frac{\kappa^{\text{fa}}\varrho^{1/2}}{\varepsilon}(c_1c_2 - c_3/\varrho)\gamma^{\text{fa}} - \kappa^{\text{sl}}\varrho^{1/2}(c_3c_4/\varrho - c_5)\gamma^{\text{sl}}.$$

The slow manifold is $\mathcal{M}_{\text{sl}} = \{c \in [0, \infty[^5 \mid c_1c_2 = c_3/\varrho\}$ and $\Gamma_{\text{fa}} = \text{span } \gamma^{\text{fa}}$. With

$$Q_{\text{fa}} = \begin{pmatrix} 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

we obtain $\mathbf{Q} = \text{im } Q_{\text{fa}} = [0, \infty[^4$. For $\mathbf{q} \in \mathbf{Q}$ it is easy to compute $\Psi_\varrho(\mathbf{q})$ as a minimizer of $c \mapsto \mathcal{E}(c)$ under the constraint $Q_{\text{fa}}c = \mathbf{q} = (q_1, \dots, q_4)$. We obtain

$$\begin{aligned} \Psi_\varrho(\mathbf{q}) &= (q_1 - a_\varrho(q_1, q_2), q_2 - a_\varrho(q_1, q_2), a_\varrho(q_1, q_2), q_3, q_4)^\top \in \mathbf{C} = [0, \infty[^5 \\ \text{with } a_\varrho(q_1, q_2) &= \frac{1}{2\varrho} \left(1 + \varrho q_1 + \varrho q_2 - \sqrt{1 + \varrho q_1 + \varrho q_2}^2 - 4\varrho^2 q_1 q_2} \right) \in [0, \min\{q_1, q_2\}]. \end{aligned}$$

In particular, the UFEC (3.5) holds. Moreover, the positivity and monotonicity condition (3.6) can be checked easily with $\bar{\mathbf{q}} = (1, 1, 1, 1)^\top$. We see that $c(\theta) := \Psi_\varrho(\mathbf{q} + \theta\bar{\mathbf{q}})$ for $\theta \in]0, 1]$ is given by

$$c(\theta) = (q_1 + \theta - a_\varrho(q_1 + \theta, q_2 + \theta), q_2 + \theta - a_\varrho(q_1 + \theta, q_2 + \theta), a_\varrho(q_1 + \theta, q_2 + \theta), q_3 + \theta, q_4 + \theta)^\top.$$

Clearly we have $c(\theta)_i > 0$, since $c(\theta)_i = 0$ would imply $q_i + \theta = 0$. Differentiating with respect to θ , we obtain

$$c'(\theta) = (1 - a'_\varrho[\theta], 1 - a'_\varrho[\theta], a'_\varrho[\theta], 1, 1)^\top \quad \text{with } a'_\varrho[\theta] = \frac{\varrho(c_1(\theta) + c_2(\theta))}{1 + \varrho(c_1(\theta) + c_2(\theta))},$$

which implies that $c'(\theta)_i > 0$. Hence, $\Psi_\varrho(\mathbf{q} + \theta\bar{\mathbf{q}})_i = c(\theta)_i \geq c(0)_i = \Psi(\mathbf{q})$, i.e. the monotonicity condition (3.6) holds.

We investigate the reduced system. First, we observe that the reduced limiting equation (4.3) is given by

$$\dot{\mathbf{q}} = Q_{\text{fa}} \mathbf{R}_{\text{sl}}(\Psi_\varrho(\mathbf{q})) = -\kappa^{\text{sl}}\varrho^{1/2} \left(\frac{a_\varrho(q_1, q_2)q_3}{\varrho} - q_4 \right) \widehat{\gamma} \quad \text{with } \widehat{\gamma} := Q_{\text{fa}}\gamma^{\text{sl}} = (1, 1, 1, -1)^\top. \quad (4.8)$$

Since a_ϱ is not a monomial, this RRE is no longer of mass-action type.

According to Section 4.1 the gradient structure $(\mathbf{Q}, E_\varrho, R_\varrho)$ for (4.8) is given via

$$\begin{aligned} E_\varrho(\mathbf{q}) &= \mathcal{E}(\Psi_\varrho(\mathbf{q})) = \lambda_{\text{B}}(q_1 - a) + \lambda_{\text{B}}(q_2 - a) + \varrho\lambda_{\text{B}}(a/\varrho) + \lambda_{\text{B}}(q_3) + \lambda_{\text{B}}(q_4) \Big|_{a=a_\varrho(q_1, q_2)}, \\ R_\varrho^*(\mathbf{q}, \zeta) &= \mathcal{R}_{\text{sl}}(\Psi_\varrho(\mathbf{q}), Q_{\text{fa}}^\top \zeta) = \kappa^{\text{sl}} (a_\varrho(q_1, q_2) q_3 q_4)^{1/2} \mathbf{C}^*(\zeta_1 + \zeta_2 + \zeta_3 - \zeta_4). \end{aligned}$$

The energy E_ϱ is no longer of Boltzmann type, because the previously uncoupled densities c_1, c_2 , and c_3 are now constrained to lie on \mathcal{M}_{sl} , i.e. $c_1 c_2 = c_3$. Nevertheless, the form is close to a mass-action type for the trimolecular reaction $Y_1 + Y_2 + Y_3 \rightleftharpoons Y_4$.

To recover an exact trimolecular reaction of mass-action type, one has to perform another limit, namely $\varrho \rightarrow 0^+$, which means that the species X_3 is no longer observed, but still exists on a microscopic reaction pathway. For the limit $\varrho \rightarrow 0^+$ we simply observe the expansion

$$a_\varrho(q_1, q_2) = \varrho q_1 q_2 + O(\varrho^2) \quad \text{for } \varrho \rightarrow 0^+,$$

which implies $\Psi_\varrho(q) \rightarrow \Psi_0(q) := (q_1, q_2, 0, q_3, q_4)^T$. If we additionally choose $\kappa^{\text{sl}} = \bar{\kappa}/\varrho^{1/2}$ and insert the expansion for a_ϱ we obtain

$$\begin{aligned} E_\varrho(q) &\rightarrow E_0(q) = \sum_{j=1}^4 \lambda_B(q_j), \\ R_\varrho^*(q, \zeta) &\rightarrow R_0^*(q, \zeta) = \bar{\kappa} (q_1 q_2 q_3 q_4)^{1/2} C^*(\zeta_1 + \zeta_2 + \zeta_3 - \zeta_4). \end{aligned}$$

Clearly, this is the gradient system generating the RRE of the trimolecular reaction $X_1 + X_2 + X_4 \rightleftharpoons X_5$. Of course, it is possible to show that this convergence is again a EDP-convergence with tilting of the gradient systems $(\mathbf{Q}, E_\varrho, R_\varrho)$ to the effective system (\mathbf{Q}, E_0, R_0) .

5 Proof of Theorem 3.4

Here we will show the Γ -convergence of the dissipation functionals, namely $\mathfrak{D}_\varepsilon \xrightarrow{M_E} \mathfrak{D}_0$. As usual the proof consists in three parts: (i) compactness of the sequences (c^ε) satisfying $\mathfrak{D}_\varepsilon(c^\varepsilon) \leq C$, (ii) the liminf estimate, and the (iii) the limsup estimate, which needs the construction of recovery sequences.

All the following results are derived under the assumptions of Theorem 3.4: The fast-slow DBRS $(A, B, c_*, \widehat{\kappa}^\varepsilon)$ satisfies the unique fast-equilibrium condition UFEC (3.5). For constructing the recovery sequence in Section 5.3, we need additionally the positivity and monotonicity assumption (3.6) for Ψ .

5.1 Compactness

In the definition of $\mathfrak{D}_\varepsilon \xrightarrow{M_E} \mathfrak{D}_0$ we consider sequences $c^\varepsilon \rightarrow c^0$ in $L^1([0, T]; \mathbf{C})$ that additionally satisfy $\sup_{\varepsilon \in]0, 1[, t \in [0, T]} \mathcal{E}(c^\varepsilon(t)) \leq C$. The aim is to extract a strongly converging subsequence $c^\varepsilon \rightarrow c^0$, such that we can talk about pointwise convergence almost everywhere. This will be necessary in the liminf estimate because we cannot rely on convexity, in contrast to the linear theory developed in [MiS19]. The compactness is derived via two quite different arguments that complement each other and reflect the underlying fast-slow structure, which is seen on the local level via the decomposition of $T_c \mathbf{C} = \mathbb{R}^{i*}$ in the direct sum of Γ_{fa} and $T_c \mathcal{M}_{\text{sl}}$, see Step 1 in the proof of Proposition 4.5. First, we derive time regularity for the slow part of the reactions. Secondly, we prove convergence towards the slow manifold which then provides the remaining information for the whole sequence.

Theorem 5.1 (Compactness via dissipation bound). *Consider $(c^\varepsilon)_{\varepsilon > 0}$ with $c^\varepsilon \rightarrow c^0$ in $L^1([0, T]; \mathbf{C})$, $\sup_{\varepsilon > 0, t \in [0, T]} \mathcal{E}(c^\varepsilon(t)) \leq M_{\text{ener}} < \infty$, and $\mathfrak{D}_\varepsilon(c^\varepsilon) \leq M_{\text{diss}} < \infty$. Then, we have*

- (i) $c^\varepsilon(\cdot)$ is bounded in $L^\infty([0, T]; \mathbf{C})$;
- (ii) $Q_{\text{fa}} c^\varepsilon \rightarrow Q_{\text{fa}} c^0$ weakly in $W^{1,1}([0, T]; \mathbb{R}^{m_{\text{fa}}})$ and strongly in $C^0([0, T]; \mathbb{R}^{m_{\text{fa}}})$;
- (iii) $c^0(t) = \tilde{c}(t) := \Psi(Q_{\text{fa}} c^0(t)) \in \mathcal{M}_{\text{sl}}$ for a.a. $t \in [0, T]$, and, in particular $\tilde{c} \in C^0([0, T], \mathbf{C})$;
- (iv) $c^\varepsilon \rightarrow c^0$ in $L^p([0, T]; \mathbf{C})$ strongly for all $p \in [1, \infty[$.

We emphasize that c^0 and \tilde{c} may be different, and this happens even for solutions, if near $t = 0$ a jump develops such that (cf. Section 2.4)

$$\lim c^\varepsilon(0) =: c_0 \neq \bar{c}_0 := \lim_{\tau \rightarrow 0^+} \left(\lim_{\varepsilon \rightarrow 0^+} c^\varepsilon(\tau) \right).$$

Before giving the detailed proof we provide two preliminary results that underpin the two complementary arguments of the proof.

For deriving bounds on the time derivatives, one heuristically sees that for fixed (c, ξ) we have $\mathcal{R}_\varepsilon^*(c, \xi) \nearrow \mathcal{R}_{\text{eff}}^*(c, \xi)$ as $\varepsilon \rightarrow 0$. By duality, this implies $\mathcal{R}_\varepsilon(c, v) \searrow \mathcal{R}_{\text{eff}}(c, v)$. This already shows that control of time derivatives has to be obtained from $\mathcal{R}_{\text{eff}}(c, \cdot)$, which only controls $Q_{\text{fa}}\dot{c}$ because $\mathcal{R}_{\text{eff}}(c, v) = \mathcal{R}_{\text{eff}}(c, w)$ if $Q_{\text{fa}}v = Q_{\text{fa}}w$, see (3.4b).

Proposition 5.2 (Effective dissipation potential). *For all $\varepsilon > 0$ we have $\mathcal{R}_\varepsilon(c, v) \geq \mathcal{R}_{\text{eff}}(c, v)$ for all $(c, v) \in \mathbf{C} \times \mathbb{R}^{i^*}$. Moreover, \mathcal{R}_{eff} takes the form*

$$\mathcal{R}_{\text{eff}}(c, v) = \tilde{\mathcal{R}}(c, Q_{\text{fa}}v) \text{ where } \tilde{\mathcal{R}}(c, \mathbf{q}) := \sup \left\{ \zeta \cdot \mathbf{q} - \mathcal{R}_{\text{sl}}^*(c, Q_{\text{fa}}^\top \zeta) \mid \zeta \in \mathbb{R}^{m_{\text{fa}}} \right\}.$$

Proof. We first use the standard relation from linear algebra: $\text{im}(Q_{\text{fa}}^\top) = (\ker(Q_{\text{fa}}))^\perp = \Gamma_{\text{fa}}^\perp$. By construction of Γ_{fa} we have $\mathcal{R}_{\text{fa}}^*(c, \xi) = 0$ for $\xi \in \Gamma_{\text{fa}}^\perp$ and obtain

$$\mathcal{R}_\varepsilon^*(c, \xi) = \mathcal{R}_{\text{sl}}^*(c, \xi) + \frac{1}{\varepsilon} \mathcal{R}_{\text{fa}}^*(c, \xi) \leq \mathcal{R}_{\text{eff}}^*(c, \xi) := \mathcal{R}_{\text{sl}}^*(c, \xi) + \chi_{\Gamma_{\text{fa}}^\perp}(\xi) = \mathcal{R}_{\text{sl}}^*(c, \xi) + \chi_{\text{im} Q_{\text{fa}}^\top}(\xi).$$

Applying the Legendre-Fenchel transformation we obtain

$$\begin{aligned} \mathcal{R}_\varepsilon(c, v) &\geq \mathcal{R}_{\text{eff}}(c, v) = \sup \left\{ v \cdot \xi - \mathcal{R}_{\text{sl}}^*(c, \xi) \mid \xi \in \text{im}(Q_{\text{fa}}^\top) \right\} \\ &= \sup \left\{ v \cdot Q_{\text{fa}}^\top \zeta - \mathcal{R}_{\text{sl}}^*(c, Q_{\text{fa}}^\top \zeta) \mid \zeta \in \mathbb{R}^{m_{\text{fa}}} \right\} = \tilde{\mathcal{R}}(c, Q_{\text{fa}}v), \end{aligned}$$

which provides the desired estimate as well as the representation via $\tilde{\mathcal{R}}$. \square

The second result concerns the convergence of points towards the slow manifold \mathcal{M}_{sl} , and the crucial property here is the UFEC (3.5) that guarantees the relation

$$\left\{ \Psi(\mathbf{q}) \mid \mathbf{q} \in \mathbf{Q} \subset \mathbb{R}^{m_{\text{fa}}} \right\} =: \mathcal{M}_{\text{sl}} \stackrel{!!}{=} \mathcal{E}_{\text{fa}} \stackrel{\text{Lemma 2.4}}{=} \left\{ c \in \mathbf{C} \mid \mathcal{S}_{\text{fa}}(c) = 0 \right\}.$$

Lemma 5.3 (Convergence towards \mathcal{M}_{sl}). *For bounded sequences $(c^n)_{n \in \mathbb{N}}$ in \mathbf{C} we have*

$$Q_{\text{fa}}c^n \rightarrow \mathbf{q} \text{ and } \mathcal{S}_{\text{fa}}(c^n) \rightarrow 0 \implies c^n \rightarrow \Psi(\mathbf{q}). \quad (5.1)$$

Proof. Without loss of generality we may assume $c^n \rightarrow \bar{c}$. Hence we have $Q_{\text{fa}}c^n \rightarrow Q_{\text{fa}}\bar{c} = \mathbf{q}$. Moreover, the continuity of \mathcal{S}_{fa} gives $0 = \lim \mathcal{S}_{\text{fa}}(c^n) = \mathcal{S}_{\text{fa}}(\bar{c})$. Thus, we have $\bar{c} \in \mathcal{E}_{\text{fa}} \cap \mathbf{C}_{\mathbf{q}}^{\text{fa}}$. Now, the UFEC (see (3.11)) gives $\bar{c} = \Psi(\mathbf{q})$ which is the desired result. \square

We are now ready to establish the main compactness result.

Proof of Theorem 5.1. Part (i): From the energy bound $\mathcal{E}(c^\varepsilon(t)) \leq M_{\text{ener}} < \infty$ and the coercivity of \mathcal{E} we obtain an L^∞ bound for c^ε , namely $0 \leq c_j^\varepsilon(t) \leq |c^\varepsilon(t)| \leq \|c^\varepsilon\|_{L^\infty} \leq M_{\text{ener}}$.

Part (ii): To provide a lower bound on \mathcal{R}_{eff} we first observe an upper bound on $\mathcal{R}_{\text{sl}}^*$, namely

$$\mathcal{R}_{\text{sl}}^*(c^\varepsilon, Q_{\text{fa}}^\top \zeta) \leq \sum_{r \in R_{\text{sl}}} \kappa_r M_{\text{ener}}^{(\alpha_r + \beta_r)/2} C^*(\gamma^r \cdot Q_{\text{fa}}^\top \zeta) \leq b_M C^*(b_Q |\zeta|) \quad \text{with } b_Q = \max_{r \in R_{\text{sl}}} |Q_{\text{fa}} \gamma^r|,$$

where we used $0 \leq c_j^\varepsilon \leq M_{\text{ener}}$ from part (i). Using the Legendre-Fenchel transformation and Proposition 5.2 we obtain the lower bound

$$\mathcal{R}_\varepsilon(c^\varepsilon, v) \geq \tilde{\mathcal{R}}(c^\varepsilon, Q_{\text{fa}} v) \geq \sup \{ Q_{\text{fa}} v \cdot \zeta - b_M C^*(b_Q |\zeta|) \mid \zeta \in \mathbb{R}^{m_{\text{fa}}} \} = b_M C\left(\frac{|Q_{\text{fa}} v|}{b_M b_Q}\right).$$

Using the bound M_{diss} for the dissipation functionals, the family satisfies

$$\int_0^T C\left(\frac{|Q_{\text{fa}} \dot{c}^\varepsilon(t)|}{b_M b_Q}\right) dt \leq \int_0^T \frac{1}{b_M} \mathcal{R}_\varepsilon(c^\varepsilon(t), \dot{c}^\varepsilon(t)) dt \leq \frac{1}{b_M} \mathfrak{D}_\varepsilon(c^\varepsilon) \leq M_{\text{diss}}/b_M.$$

Since $C(s) \geq \frac{1}{2}|s| \log(1+|s|)$ for all $s \in \mathbb{R}$ (cf. [MiS19, Eqn. (A.2)]) we have a uniform super-linear bound for $Q_{\text{fa}} \dot{c}^\varepsilon$. Thus, there exists a subsequence (not relabeled) such that $Q_{\text{fa}} \dot{c}^\varepsilon \rightharpoonup w$ in $L^1([0, T]; \mathbb{R}^{m_{\text{fa}}})$. Moreover, $Q_{\text{fa}} c^\varepsilon$ is equicontinuous (cf. [MiS19, Prop. 5.9]), which implies $Q_{\text{fa}} c^\varepsilon \rightarrow q^0$ in $C^0([0, T]; \mathbf{Q})$.

Because of $c^\varepsilon \rightharpoonup c^0$ we conclude $q^0 = Q_{\text{fa}} c^0 \in W^{1,1}([0, T]; \mathbf{Q})$ and $\dot{q} = w$. Since the limit is unique, we also know that the whole family converges.

Part (iii): The dissipation bound gives the estimate $\int_0^T \mathcal{S}_{\text{fa}}(c^\varepsilon(t)) dt \leq \varepsilon M_{\text{diss}}$. Using $\mathcal{S}_{\text{fa}}(c) \geq 0$ this implies that $f_\varepsilon = \mathcal{S}_{\text{fa}} \circ c^\varepsilon$ converges to 0 in $L^1([0, T])$. Thus, we may choose a subsequence (not relabeled) such that $f_\varepsilon(t) \rightarrow 0$ a.e. in $[0, T]$.

By the continuity \mathcal{S}_{fa} and $|c^\varepsilon(t)| \leq M_{\text{ener}}$ we also know that $(f_\varepsilon(t))_{\varepsilon \in]0, 1[}$ is bounded, while part (ii) provides the convergence $Q_{\text{fa}} c^\varepsilon(t) \rightarrow q^0(t) = Q_{\text{fa}} c^0(t)$. Hence, Lemma 5.3 guarantees $c^\varepsilon(t) \rightarrow \tilde{c}(t) := \Psi(Q_{\text{fa}} c^0(t))$ a.e. in $[0, T]$. By $c^\varepsilon \rightharpoonup c^0$ we have $c^0(t) = \tilde{c}(t)$ a.e.

Since Ψ is continuous by Proposition 3.6, also $\tilde{c} = \Psi(Q_{\text{fa}} c^0)$ is continuous.

Part (iv): This follows via part (i), the pointwise a.e. convergence established in the proof of part (iii), and from the dominated-convergence theorem. \square

5.2 Liminf estimate

The liminf estimate follows in a straightforward manner by using the fact that the velocity part \mathcal{R}_ε in \mathfrak{D}_ε satisfies the monotonicity $\mathcal{R}_\varepsilon \geq \mathcal{R}_{\text{eff}}$, see Proposition 5.2, and that the slope part \mathcal{S}_ε takes the simple form $\mathcal{S}_{\text{sl}} + \frac{1}{\varepsilon} \mathcal{S}_{\text{fa}}$.

Theorem 5.4 (Liminf estimate). *Let $(c^\varepsilon)_{\varepsilon > 0}$ with $c^\varepsilon \rightharpoonup c^0$ in $L^1([0, T]; \mathbf{C})$ as in Theorem 5.1 we have the estimate $\mathfrak{D}_0(c^0) \leq \liminf_{\varepsilon \rightarrow 0^+} \mathfrak{D}_\varepsilon(c^\varepsilon)$.*

Proof. We may assume that $\alpha_* := \liminf_{\varepsilon \rightarrow 0} \mathfrak{D}_\varepsilon(c^\varepsilon) < \infty$, since otherwise the desired estimate is trivially satisfied. This implies $\mathcal{S}_{\text{fa}}(c^0(t)) = 0$ a.e. in $[0, T]$ as in the previous proof. We define the functional

$$\mathfrak{I}(c, q) := \int_0^T \mathcal{F}(c(t), q(t)) dt \quad \text{with } \mathcal{F}(c, w) = \tilde{\mathcal{R}}(c, w) + \mathcal{S}_{\text{sl}}(c).$$

Then, using $\mathcal{R}_\varepsilon \geq \mathcal{R}_{\text{eff}}$ and $\mathcal{S}_\varepsilon \geq \mathcal{S}_{\text{sl}}$, we have

$$\mathfrak{D}_\varepsilon(c^\varepsilon) \geq \mathfrak{I}(c^\varepsilon, Q_{\text{fa}}\dot{c}^\varepsilon) \quad \text{and} \quad \mathfrak{D}_0(c^0) = \mathfrak{I}(c^0, Q_{\text{fa}}\dot{c}^0),$$

where the last identity follows from the construction of the density \mathcal{F} via $\tilde{\mathcal{R}}$ and \mathcal{S}_{sl} , and $\mathcal{S}_0(c(t)) = \mathcal{S}_{\text{sl}}(c(t))$ a.e. because of $\mathcal{S}_{\text{fa}}(c^0(t)) = 0$.

Thus, it suffices to show the lower semicontinuity $\mathfrak{I}(c^0, Q_{\text{fa}}\dot{c}^0) \leq \liminf_{\varepsilon \rightarrow 0^+} \mathfrak{I}(c^\varepsilon, Q_{\text{fa}}\dot{c}^\varepsilon)$. Using the strong convergence $c^\varepsilon \rightarrow c^0$ in $L^p([0, T]; \mathbf{C})$ and the weak convergence $Q_{\text{fa}}\dot{c}^\varepsilon \rightharpoonup Q_{\text{fa}}\dot{c}^0$ in $L^1([0, T]; \mathbb{R}^{m_{\text{fa}}})$, see Theorem 5.1(ii+iv), this follows by Ioffe's theorem (cf. [FoL07, Thm. 7.5] if we know that $\mathcal{F} : \mathbf{C} \times \mathbb{R}^{m_{\text{fa}}} \rightarrow [0, \infty]$ is lower semicontinuous. However, the lower semicontinuity of $(c, w) \mapsto \mathcal{F}(c, w) = \tilde{\mathcal{R}}(c, w) + \mathcal{S}_{\text{sl}}(c)$ follows immediately from the continuity of \mathcal{S}_{sl} and the by Legendre transforming the continuous function $(c, \zeta) \mapsto \mathcal{R}_{\text{sl}}^*(c, Q_{\text{fa}}^\top \zeta)$.

This finishes the proof of Theorem 5.4. \square

5.3 Construction of the recovery sequence

In this section we construct the recovery sequence which completes the proof of the Mosco convergence $\mathfrak{D}_\varepsilon \xrightarrow{M_E} \mathfrak{D}_0$ with energy constraint. Below in Step 1, we will need the positivity and monotonicity condition (3.6) for $\theta \mapsto \Psi(q + \theta\bar{q})$.

Theorem 5.5 (Limsup estimate). *Let $c^0 \in L^1([0, T]; \mathbf{C})$ with $\sup_{t \in [0, T]} \mathcal{E}(c^0(t)) < \infty$. Then there exists a family $(c^\varepsilon)_{\varepsilon \in]0, 1]}$ with $\sup_{t \in [0, T], \varepsilon \in]0, 1]} \mathcal{E}(c^\varepsilon(t)) \leq M_{\text{ener}} < \infty$, $c^\varepsilon \rightarrow c^0$ strongly in $L^1([0, T]; \mathbf{C})$, and $\lim_{\varepsilon \rightarrow 0} \mathfrak{D}_\varepsilon(c^\varepsilon) = \mathfrak{D}_0(c^0)$.*

Proof. We prove the theorem in several steps. In Steps 1 and 2 we show that it is sufficient to consider $c^0 \in W^{1, \infty}([0, T]; \mathbf{C})$ with $c_j^0(t) \geq \underline{c} > 0$, where we only work in \mathfrak{D}_0 which has the advantage that $\mathcal{R}_{\text{eff}}(c, \dot{c})$ only depends on $(q, \dot{q}) = (Q_{\text{fa}}c, Q_{\text{fa}}\dot{c})$, see Section 4.1. In Step 3 we construct a recovery sequence, and in Step 4 we conclude with a diagonal argument.

Step 0: To start with we may assume $\mathfrak{D}_0(c^0) < \infty$. Indeed, if $\mathfrak{D}_0(c^0) = \infty$, then we choose $c^\varepsilon = c^0$ and Theorem 5.4 gives $\liminf_{\varepsilon \rightarrow 0} \mathfrak{D}_\varepsilon(c^\varepsilon) \geq \mathfrak{D}_0(c^0) = \infty$, which means $\mathfrak{D}_\varepsilon(c^\varepsilon) \rightarrow \infty$ as desired.

Step 1. Reducing to positive curves c^0 : For c^0 with $\mathfrak{D}_0(c^0) < \infty$ we have $Q_{\text{fa}}c^0 \in W^{1, 1}([0, T]; \mathbf{Q})$ and $c^0 \in C^0([0, T]; \mathbf{C})$ after choosing the continuous representative $c^0 = \tilde{c}$, see Theorem 5.1. Exploiting the positivity and monotonicity condition (3.6) we now set

$$\underline{c}^l(t) := \Psi(q(t) + \theta_l \bar{q}) \quad \text{with} \quad \theta_l = \frac{1}{l+1} \in]0, 1[\quad \text{for all } t \in [0, T].$$

By this condition, we know that $\underline{c}^l(t)$ lies in \mathbf{C}_+ for all $t \in [0, T]$, such that the continuity of \underline{c}^l guarantees that for each l there exists a $\delta_l > 0$ such that $\underline{c}_i^l(t) \geq \delta_l$ for all $i \in I$ and $t \in [0, T]$.

By the continuity of Ψ we have $\underline{c}^l \rightarrow c^0$ uniformly and hence strongly in $L^1([0, T]; \mathbf{C})$. We now show

$$\mathfrak{D}_0(\underline{c}^l) = \int_0^T \{ \mathcal{R}_{\text{eff}}(\underline{c}^l(t), \dot{\underline{c}}^l(t)) + \mathcal{S}_0(\underline{c}^l(t)) \} dt \rightarrow \mathfrak{D}_0(c^0) \quad \text{as } l \rightarrow 0. \quad (5.2)$$

For the second part, we use $\underline{c}^l(t) \in \mathcal{M}_{\text{sl}}$ by construction via Ψ , and the continuity of \mathcal{S}_{sl} yields $\mathcal{S}_0(\underline{c}^l(t)) = \mathcal{S}_{\text{sl}}(\underline{c}^l(t)) \rightarrow \mathcal{S}_{\text{sl}}(c^0(t)) = \mathcal{S}_0(c^0(t))$ uniformly in $[0, T]$.

For the first part we use (i) the special form of \mathcal{R}_{eff} derived in Proposition 5.2, namely $\mathcal{R}_{\text{eff}}(c, v) = \tilde{\mathcal{R}}(c, Q_{\text{fa}}v)$, where $\tilde{\mathcal{R}}(c, \cdot)$ is the Legendre transform of $\mathcal{R}_{\text{sl}}^*(c, Q^\top \cdot)$. Moreover, the cosh-type dual dissipation potential $\mathcal{R}_{\text{sl}}^*$ as defined in (2.6b) or (2.14) enjoys (ii) a monotonicity property namely $\mathcal{R}_{\text{sl}}^*(c, \xi) \leq \mathcal{R}_{\text{sl}}^*(\tilde{c}, \xi)$ or equivalently $\mathcal{R}_{\text{sl}}(c, v) \geq \mathcal{R}_{\text{sl}}(\tilde{c}, v)$ if $c \leq \tilde{c}$ componentwise. This can be exploited because of the monotonicity condition (3.6) using $\underline{c}^l(t) \geq c^0(t)$ componentwise. With $Q_{\text{fa}} \dot{c}^l(t) = \dot{q}(t)$ for all $l \in \mathbb{N}$ we obtain

$$\int_0^T \mathcal{R}_{\text{eff}}(\underline{c}^l, \dot{c}^l(t)) dt \stackrel{(i)}{=} \int_0^T \tilde{\mathcal{R}}(\underline{c}^l, \dot{q}(t)) dt \xrightarrow{(ii)} \int_0^T \tilde{\mathcal{R}}(c^0, \dot{q}(t)) dt \stackrel{(i)}{=} \int_0^T \mathcal{R}_{\text{eff}}(c^0, \dot{c}^0) dt,$$

where the convergence $\xrightarrow{(ii)}$ follows from the dominated-convergence theorem, since the integrands on the left-hand side are bounded by that on the right-hand side and we have pointwise convergence. With this we have established the desired convergence (5.2).

Step 2. Reducing to bounded derivative $\dot{q} = Q_{\text{fa}}\dot{c}$: Because of Step 1, we can now assume

$$c^0(t) \in \mathbf{C}_\delta := \{c \in \mathbf{C} \mid |c| \leq 1/\delta, c_i \geq \delta \text{ for all } i \in I\} \text{ for all } t \in [0, T]$$

where $\delta > 0$. Moreover, as in [MiS19, Step 2(b) of proof of Thm. 5.12] we find Λ^* such that

$$c, \tilde{c} \in \mathbf{C}_\delta \text{ and } |c - \tilde{c}| \leq \alpha < \frac{1}{2\Lambda^*} \implies \tilde{\mathcal{R}}(\tilde{c}, w) \leq (1 + \Lambda^*\alpha) \tilde{\mathcal{R}}(c, w).$$

With this we can estimate $\mathcal{R}_{\text{sl}}^*(c, \cdot)$ from below and hence \mathcal{R}_{eff} from above. Moreover, we can use the Lipschitz continuity of $c \mapsto \mathcal{R}_\varepsilon^*$.

For $q(t) = Q_{\text{fa}}c^0 \in W^{1,1}([0, T]; \mathbf{Q})$ we define the piecewise affine interpolants \hat{q}^k via

$$\hat{q}^k((n+\theta)2^{-k}T) = (1-\theta)q(n2^{-k}T) + \theta q((n+1)2^{-k}T) \text{ for } \theta \in [0, 1], n \in \{0, \dots, 2^k - 1\}$$

and the piecewise constant interpolant $\bar{q}^k((n+\theta)2^{-k}T) = q(2^{-k}nT)$ for $\theta \in [0, 1[$. We also set $\hat{c}^k(t) = \Psi(\hat{q}^k(t))$ and $\bar{c}^k(t) = \Psi(\bar{q}^k(t))$. By standard arguments we have

$$\|\bar{c}^k - \hat{c}^k\|_{L^\infty} + \|\hat{c}^k - c^0\|_{L^\infty} =: \alpha_k \rightarrow 0 \text{ for } k \rightarrow \infty.$$

As in Step 1 we again find $\int_0^T \mathcal{S}_0(\hat{c}^k(t)) dt \rightarrow \int_0^T \mathcal{S}_0(c^0(t)) dt$. To treat the velocity part we use both interpolants obtain the estimate

$$\begin{aligned} \int_0^T \mathcal{R}_{\text{eff}}(\hat{c}^k, \dot{\hat{c}}^k) dt &= \int_0^T \tilde{\mathcal{R}}(\hat{c}^k, \dot{\hat{q}}^k) dt \leq (1 + \Lambda^*\alpha_k) \int_0^T \tilde{\mathcal{R}}(\bar{c}^k, \dot{\hat{q}}^k) dt \\ &\stackrel{(J)}{\leq} (1 + \Lambda^*\alpha_k) \int_0^T \tilde{\mathcal{R}}(\bar{c}^k, \dot{q}) dt \leq \int_0^T \tilde{\mathcal{R}}(c^0, \dot{q}) dt = (1 + \Lambda^*\alpha_k)^2 \int_0^T \mathcal{R}_{\text{eff}}(c^0, \dot{c}^0) dt, \end{aligned}$$

where $\stackrel{(J)}{\leq}$ indicates the use of Jensen's inequality applied to the convex integrand $\tilde{\mathcal{R}}(\bar{c}^k(t), \cdot)$, which is independent of t in the intervals $]2^{-k}nT, 2^{-k}(n+1)T[$. Combining this with the slope part and using $\alpha_k \rightarrow 0$ we obtain the desired estimate $\limsup_{k \rightarrow \infty} \mathfrak{D}_0(\hat{c}^k) \leq \mathfrak{D}_0(c^0)$, which is of course a limit because of the liminf estimate in Theorem 5.4.

Step 3. The limsup for $\varepsilon \rightarrow 0^+$: By Steps 1 and 2 it is sufficient to consider $c^0 \in W^{1,\infty}([0, T]; \mathbf{C})$ with $c^0(t) = \Psi(q(t)) \in \mathbf{C}_\delta$ for some $\delta > 0$. For these functions we can now use the constant recovery sequence $c^\varepsilon = c^0$, i.e. we will show

$$\mathfrak{D}_\varepsilon(c^0) = \int_0^T \{\mathcal{R}_\varepsilon(c^0, \dot{c}^0) + \mathcal{S}_\varepsilon(c^0)\} dt \rightarrow \mathfrak{D}_0(c^0) = \int_0^T \{\mathcal{R}_{\text{eff}}(c^0, \dot{c}^0) + \mathcal{S}_0(c^0)\} dt \quad (5.3)$$

for $\varepsilon \rightarrow 0^+$. Because of $c^0(t) \in \mathcal{M}_{\text{sl}}$ we have $\mathcal{S}_\varepsilon(c^0(t)) = \mathcal{S}_{\text{sl}}(c^0(t)) = \mathcal{S}_0(c^0(t))$, so the second summand of the integral $\mathfrak{D}_\varepsilon(c^0)$ converges trivially.

Recall that $\Gamma = \text{span} \{ \gamma^r \mid r \in R = R_{\text{sl}} \dot{\cup} R_{\text{fa}} \}$ and define a projection \mathbb{Q} on \mathbb{R}^{i^*} with $\text{im } \mathbb{Q} = \Gamma$ giving $\ker \mathbb{Q}^\top = \Gamma^\perp$. With this we can estimate the dual dissipation potential $\mathcal{R}_\varepsilon^*$ from below:

$$\mathcal{R}_\varepsilon^*(c, \xi) \geq \mathcal{R}_1^*(c, \xi) \geq b_* |\mathbb{Q}^\top \xi|^2.$$

To see this use $C^*(\sigma) \geq \frac{1}{2}\sigma^2$ and $(c^{\alpha r} c^{\beta r})^{1/2} \geq \delta^{(\alpha r + \beta r)/2}$ for all $r \in R$.

By Legendre-Fenchel transformation we obtain an upper bound for \mathcal{R}_ε , where we use $\dot{c}^0 \in \Gamma$, i.e. $\mathbb{Q}\dot{c}^0(t) = \dot{c}^0(t)$ (cf. Lemma 2.5):

$$\mathcal{R}_\varepsilon(c^0(t), \dot{c}^0(t)) \leq \mathcal{R}_1(c^0(t), \dot{c}^0(t)) \leq \frac{1}{4b_*} |\mathbb{Q}\dot{c}^0(t)|^2 = \frac{1}{4b_*} |\dot{c}^0(t)|^2.$$

From $c^0 \in W^{1,\infty}([0, T]; \mathbf{C})$ we see that $t \mapsto \mathcal{R}_1(c^0(t), \dot{c}^0(t))$ lies in $L^\infty([0, T])$ and thus provides an integrable majorant for $t \mapsto \mathcal{R}_\varepsilon(c^0(t), \dot{c}^0(t))$. However, the convergence $\mathcal{R}_\varepsilon^*(c, \xi) \nearrow \mathcal{R}_0^* = \mathcal{R}_{\text{sl}}^* + \chi_{\Gamma_{\text{fa}}^\perp}$ for $\varepsilon \rightarrow 0^+$ implies $\mathcal{R}_\varepsilon(c, v) \searrow \mathcal{R}_{\text{eff}}(c, v)$ for all $(c, v) \in \mathbf{C}_\delta \times \mathbb{R}^{i^*}$. Hence, Lebesgue's dominated convergence theorem gives

$$\int_0^T \mathcal{R}_\varepsilon(c^0(t), \dot{c}^0(t)) dt \rightarrow \int_0^T \mathcal{R}_{\text{eff}}(c^0(t), \dot{c}^0(t)) dt \quad \text{for } \varepsilon \rightarrow 0^+,$$

and (5.3) is established.

Step 4. Diagonal sequence: The full recovery sequence for a general c^0 with $\mathfrak{D}_0(c^0) < \infty$ is obtained via $q(t) = Q_{\text{fa}} c^0(t)$ as a diagonal sequence $c^\varepsilon = \Psi(\widehat{q}^{k(\varepsilon)}(t) + \theta_{l(\varepsilon)} \bar{q})$, where the functions $k(\varepsilon)$ and $l(\varepsilon)$ are suitably chosen such that $c^\varepsilon \rightarrow c^0$ strongly in $L^1([0, T]; \mathbf{C})$ and $\mathfrak{D}_\varepsilon(c^\varepsilon) \rightarrow \mathfrak{D}_0(c^0)$. It is also clear from the construction that $\|c^\varepsilon\|_{L^\infty} \leq 1 + \|c^0\|_{L^\infty}$ such that the uniform energy bound $\mathcal{E}(c^\varepsilon(t)) \leq M_{\text{ener}}$ holds. \square

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