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Thermomechanical modeling of energy-reaction-diffusion systems, including bulk-interface interactions

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Dedicated to Michel Frémond on the occasion of his seventieth birthday

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Abstract

We show that many couplings between parabolic systems for processes in solids can be formulated as a gradient system with respect to the total free energy or the total entropy. This includes Allen-Cahn, Cahn-Hilliard, and reaction-diffusion systems and the heat equation. For this, we write the coupled system as an Onsager system $(\boldsymbol{X}, \Phi, \mathcal{K})$ defining the evolution $\dot{U} = -\mathcal{K}(U)\mathrm{D}\Phi(U)$. Here Φ is the driving functional, while the Onsager operator $\mathcal{K}(U)$ is symmetric and positive semidefinite. If the inverse $\mathcal{G} = \mathcal{K}^{-1}$ exists, the triple $(\boldsymbol{X}, \Phi, \mathcal{G})$ defines a gradient system.

Onsager systems are well suited to model bulk-interface interactions by using the dual dissipation potential $\Psi^*(U, \Xi) = \frac{1}{2}\langle \Xi, \mathcal{K}(U)\Xi \rangle$. Then, the two functionals Φ and Ψ^* can be written as a sum of a volume integral and a surface integral, respectively. The latter may contain interactions of the driving forces in the interface as well as the traces of the driving forces from the bulk. Thus, capture and escape mechanisms like thermionic emission appear naturally in Onsager systems, namely simply through integration by parts.

1 Introduction

The aim of this work is to present a unifying thermomechanical framework for the modeling of dissipative effects in solids. In particular, this will allow us to derive thermodynamically consistent couplings between several effects usually considered separately. This will include Allen-Cahn and Cahn-Hilliard systems for vectors of phase indicators and the dissipative evolution of internal variables like viscoplasticity or magnetization. Moreover, reaction-diffusion system of mass-action type can also be handled. Most importantly, the coupling to the energy balance (heat equation) is discussed in detail to obtain a correct energy balance and a positive entropy-production rate.

The main idea of the paper is to formulate all these processes in terms of a gradient system. For most of the individual systems the gradient structure is well established and used in different occasions. For reaction-diffusion system a full gradient structure was established only recently in [Mie11b], including the non-isothermal case with a heat equation. However, the coupling of different gradient systems is nontrivial, and the main observation of this paper is that the coupling is largely simplified if we consider the dual formulations, which we call *Onsager systems*.

A gradient system is a triple $(\boldsymbol{X}, \Phi, \mathcal{G})$, where $\boldsymbol{X}$ is the state space, $\Phi : \boldsymbol{X} \to \mathbb{R}$ is the energy functional driving the dynamics, and $\mathcal{G}$ is a metric tensor, i.e. $\mathcal{G}(U) : \mathrm{T}_U\boldsymbol{X} \to \mathrm{T}_U^*\boldsymbol{X}$ is a symmetric and positive (semi)definite operator, which is called the Riemannian tensor (if $\boldsymbol{X}$ is a finite-dimensional manifold). The evolution equation is given by

$$\mathcal{G}(U)\dot{U} = -\mathrm{D}\Phi(U).$$

In many cases an Onsager system $(\boldsymbol{X}, \Phi, \mathcal{K})$ is equivalent to a gradient system, as its equation is

$$\dot{U} = -\mathcal{K}(U)\mathrm{D}\Phi(U), \tag{1.1}$$

and now $\mathcal{K}(U) : \mathrm{T}_U^*\boldsymbol{X} \to \mathrm{T}_U\boldsymbol{X}$ is a symmetric and positive semidefinite operator. Clearly, if $\mathcal{G}$ and $\mathcal{K}$ are invertible the two notions are equivalent by setting $\mathcal{K}(U) = \mathcal{G}(U)^{-1}$. We call the triple $(\boldsymbol{X}, \Phi, \mathcal{K})$ an Onsager system, because of Onsager's fundamental symmetry

relations, meaning $\mathcal{K} = \mathcal{K}^*$, and the *Onsager principle*. The latter states that the rate $\dot{U}$ of a macroscopic variable U is given by the product of a symmetric matrix (the activities) and the thermodynamically conjugate driving force, namely $-\mathrm{D}\Phi(U)$. The similar theory for fluxes (cf. [Ons31]) states that the mobility tensor $\mathbb{M}$ in diffusive system must be symmetric, see Sections 2.2 and 3.2.1.

From the thermodynamical point of view, we will consider two distinct cases, the isothermal and the non-isothermal case. In the former case the free energy $\mathcal{F}(\boldsymbol{y}) = \mathcal{E}(\boldsymbol{y}, \theta_*) - \theta_* \mathcal{S}(\boldsymbol{y}, \theta_*)$ is the driving potential Φ. In the non-isothermal case we will use the state variable $(\boldsymbol{y}, r)$ where r is a scalar temperature-like variable, which is typically chosen to be the temperature θ, the internal energy density e, or the entropy density s. Since we are dealing with a closed system, we have the total energy $\mathcal{E}(\boldsymbol{y}, r)$ as a conserved functional while the negative total entropy $-\mathcal{S}(\boldsymbol{y}, r)$ serves as the driving functional Φ. Note that the corresponding Onsager operators $\mathcal{K}_{\mathrm{isoth}}(\boldsymbol{y})$ and $\mathcal{K}_{\mathrm{noniso}}(\boldsymbol{y}, r)$ have different physical dimensions, the former defining the dual dissipation potential $\Psi^*_{\mathrm{isoth}}(\boldsymbol{y}; \boldsymbol{\eta}) = \frac{1}{2}\langle \boldsymbol{\eta}, \mathcal{K}_{\mathrm{isoth}}(\boldsymbol{y})\boldsymbol{\eta}\rangle$ and the latter defining the dual entropy-production potential $\Psi^*_{\mathrm{noniso}}(\boldsymbol{y}, r; \boldsymbol{\eta}, \tau) = \frac{1}{2}\langle \binom{\boldsymbol{\eta}}{\tau}, \mathcal{K}_{\mathrm{noniso}}(\boldsymbol{y}, r)\binom{\boldsymbol{\eta}}{\tau}\rangle$.

The advantages of the Onsager form over the gradient systems are manifold. First, we are used to write ordinary and partial differential equations as rate equations $\dot{U} = ...$, where the right-hand side is often a sum of different terms relating to different physical effects. Such a structure can easily be mimicked in Onsager system, by writing

$$\dot{U} = -\big(\mathcal{K}_1(U) + \mathcal{K}_2(U) + \cdots + \mathcal{K}_N(U)\big)\mathrm{D}\Phi(U).$$

Thus, we can add different dissipation mechanisms as long as we use the same driving functional, namely the physical free energy or the negative entropy. This provides a natural way to add diffusive and reactive effects of chemical species, thermal entropy production, or dissipation through changing phase indicators.

A second advantage of the Onsager systems is that differential operators for the $\mathcal{K}_j$ can easily be handled, like in the case of the Cahn-Hilliard equation, the heat equation, or in diffusion systems. Most efficiently $\mathcal{K}$ is defined in terms of the dual dissipation potential $\Psi^*(U, \Xi) = \frac{1}{2}\langle \Xi, \mathcal{K}(U)\Xi\rangle$ for the isothermal case (and the dual entropy-production potential for the non-isothermal case), i.e. $\mathcal{K}$ is defined in terms of a nonnegative quadratic form.

Third, it is easy to handle linear and nonlinear conserved quantities such as the total energy $\mathcal{E}$ in the case of closed non-isothermal systems. We simply have to ask $\mathcal{K}(U)\mathrm{D}\mathcal{E}(U) \equiv 0$ to obtain $\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{E}(U(t)) = 0$ along solutions of $\dot{U} = -\mathcal{K}(U)\mathrm{D}\Phi(U)$.

The structure of the paper is the following. In Section 2 we provide definitions and motivations for gradient and Onsager systems and discuss their relation. In particular, we address the isothermal case and the non-isothermal cases. In Section 3 we exhibit the Onsager structure in a series of bulk models such as the Allen-Cahn equation, the Cahn-Hilliard equation, the heat equation, and the Penrose-Fife model. In Section 2.4 we highlight that for energy-preserving and entropy-driven systems the *free entropy* (rather than the free energy) is the quantity defining the effective driving forces. Section 3.2 follows [Mie11b], where an Onsager structure for reaction-diffusion systems is established for reaction systems satisfying the detailed balance condition. While Section 3.3 treats isothermal couplings between several bulk effects, the Onsager structure for non-isothermal cases is addressed in Section 3.4, in particular for energy-reaction-diffusion systems.

Finally, in Section 4 we study the interaction between bulk effects and interface effects, where the framework of Onsager systems proves to be very efficient. As in [Bed86, KjB08] we use bulk fields $\boldsymbol{z} : \Omega \to \mathbb{R}^m$ and interface fields $\boldsymbol{z}_\Gamma : \Gamma \to \mathbb{R}^k$ and define the state as $Z = (\boldsymbol{z}, \boldsymbol{z}_\Gamma)$. We define functionals Φ and Ψ^* that consist of a bulk integrals and interface integrals. Then, the Onsager system $\dot{Z} = -\mathrm{D}_\Xi \Psi^*(Z; \mathrm{D}\Phi(Z))$ can be obtained by simple variational derivative involving suitable integrations by part. We obtain consistent systems with interface dynamics coupled via boundary interface conditions to the bulk dynamics, cf. [Bed86, KjB08] for the physical relevance of these systems. Section 4.4 presents an application in photovoltaics, which is treated in more detail in [GlM11].

2 Gradient systems versus Onsager systems

In this section we give some general background about gradient systems and Onsager systems. All our arguments are formal and assume sufficient smoothness of the potentials and the solutions, which is the common approach in thermomechanical modeling.

2.1 Gradient systems

A gradient system is a triple $(\boldsymbol{X}, \Phi, \mathcal{G})$ where $\boldsymbol{X}$ is the state space containing the states $U \in \boldsymbol{X}$. For simplicity we assume that $\boldsymbol{X}$ is a reflexive Banach space with dual $\boldsymbol{X}^*$. The driving functional $\Phi : \boldsymbol{X} \to \mathbb{R}_\infty := \mathbb{R} \cup \{\infty\}$ is assumed to be differentiable (in a suitable way) such that the potential restoring force is given by $-\mathrm{D}\Phi(U) \in \boldsymbol{X}^*$. The third ingredient is a metric tensor $\mathcal{G}$, i.e. $\mathcal{G}(U) : \boldsymbol{X} \to \boldsymbol{X}^*$ is linear, symmetric and positive (semi-)definite.

The gradient flow associated with $(\boldsymbol{X}, \Phi, \mathcal{G})$ is the (abstract) force balance

$$\mathcal{G}(U)\dot{U} = -\mathrm{D}\Phi(U) \qquad \Longleftrightarrow \qquad \dot{U} = -\nabla_{\mathcal{G}}\Phi(U), \tag{2.1}$$

where we recall that the "gradient" $\nabla_{\mathcal{G}}\Phi$ of the functional Φ is an element of $\boldsymbol{X}$ (in contrast to the differential $\mathrm{D}\Phi(U) \in \boldsymbol{X}^*$) and is calculated via $\mathcal{G}(U)^{-1}\mathrm{D}\Phi(U)$. We call this equation an abstract force balance, since $\mathcal{G}(U)\dot{U}$ can be seen as a viscous force arising from the motion of U. In fact, the symmetry of $\mathcal{G}$ allows us to define a *dissipation potential* $\Psi : \boldsymbol{X} \times \boldsymbol{X} \to [0, \infty]$ via

$$\Psi(U, V) = \frac{1}{2}\langle \mathcal{G}(U)V, V \rangle.$$

The symmetry of $\mathcal{G}$ implies that $\mathrm{D}_V \Psi(U, V) = \mathcal{G}(U)V$.

2.2 Onsager systems

The importance of gradient systems has its major basis in thermodynamics (TD), namely in *Onsager's symmetry relations* or more general in *Onsager's principle*, see [Ons31, DeM84]. Strictly speaking, this principle is only derived for systems close to thermodynamic equilibrium and has two forms, both of which are relevant in the present work. In the first case one considers a spatially homogeneous system described by a state vector z, which is a small perturbation of the equilibrium. Then, its macroscopic rate $\dot{z}$ is given in the form $K\zeta$, where $\zeta = \mathrm{D}S(z)$ is the thermodynamically conjugate driving force and

S is the entropy. The symmetry relation states that the matrix K has to be symmetric, while the entropy production principle $\frac{\mathrm{d}}{\mathrm{d}t}S(z(t) = \mathrm{D}S(z) \cdot K\mathrm{D}S(z) \geq 0$ implies that K has to be positive semidefinite.

In the second case one considers a spatially extended system with densities $u_i > 0$ defining a vector $\boldsymbol{u} = (u_i)_{i=1,\dots,I} : \Omega \to]0,\infty[^I$ and a total entropy $\mathcal{S}(\boldsymbol{u}) = \int_\Omega S(x, \boldsymbol{u}(x))\,\mathrm{d}x$. If the total $m_i := \int_\Omega u_i(x)\,\mathrm{d}x$ is conserved, then the densities satisfy a balance equation in the form

$$\dot{\boldsymbol{u}} + \operatorname{div} \boldsymbol{j}_{\boldsymbol{u}} = 0 \quad \text{with a flux vector} \quad \boldsymbol{j}_{\boldsymbol{u}} = \mathbb{M}\nabla\boldsymbol{\mu},$$

where the vector $\boldsymbol{\mu}$ of the chemical potentials is given by $\boldsymbol{\mu} = \mathrm{D}\mathcal{S}(\boldsymbol{u})$, i.e. $\mu_i(x) = \partial_{u_i} S(x, u(x))$. Again the symmetry and entropy principle state that $\mathbb{M}$ is a symmetric and positive semidefinite tensor (of fourth order), see [Ons31].

Note that in this work we will call $\boldsymbol{\mu} = \mathrm{D}\mathcal{S}$ the thermodynamic driving force (rather than a potential), while others call the components μ_i of $\boldsymbol{\mu}$ the chemical potentials (for the gradients $\nabla\mu_j$). In this work a driving force is lying in the dual space of the variable (here $\boldsymbol{u}$), while $\nabla\mu_j$ relates to gradient in the physical domain Ω. However, more importantly, we will group the equation $\dot{\boldsymbol{u}} + \operatorname{div}\left(\mathbb{M}\nabla\boldsymbol{\mu}\right) = 0$ with $\boldsymbol{\mu} = \mathrm{D}S$ in the form $\dot{\boldsymbol{u}} = \mathcal{K}(\boldsymbol{u})\mathrm{D}S$, where $\mathcal{K}(\boldsymbol{u}) = -\operatorname{div}\left(\mathbb{M}\nabla\square\right)$ is a symmetric operator.

We combine the thermodynamic considerations into an abstract form and use them even further away from the thermodynamic equilibrium, see [Ött05] for physical justifications to use these principles beyond the range of linear irreversible TD. In conclusion we call a triple $(\boldsymbol{X}, \Phi, \mathcal{K})$ an *Onsager system*, if $\Phi : \boldsymbol{X} \to \mathbb{R}_\infty$ is a functional and $\mathcal{K}(U) : \boldsymbol{X}^* \to \boldsymbol{X}$ is a linear, symmetric, and positive semidefinite operator. Of course, $\mathcal{K}$ may also be an unbounded operator defined on a suitable subset of $\boldsymbol{X}^*$. The evolution of the states U is given via

$$\dot{U} = -\mathcal{K}(U)\mathrm{D}\Phi(U). \tag{2.2}$$

In duality to the case of gradient systems we define a dual dissipation potential

$$\Psi^*(U, \Xi) = \frac{1}{2}\langle \Xi, \mathcal{K}(U)\Xi \rangle,$$

such that (2.2) takes the form $\dot{U} = \mathrm{D}_\Xi \Psi^*(U, -\mathrm{D}\Phi(U))$.

Interpreting the metric $\mathcal{G}$ and the Onsager operator $\mathcal{K}$ in the appropriate way, there is a one-to-one correspondence between gradient systems and Onsager systems. This equivalence is most easily seen by using the Legendre transform for relating the dissipation potential $\Psi(U, \dot{U})$ of the gradient system $(\boldsymbol{X}, \Phi, \mathcal{G})$ to the dual dissipation potential $\Psi^*(U, \Xi)$ of the Onsager system $(\boldsymbol{X}, \Phi, \mathcal{K})$. For this we extend Ψ and Ψ^* by the value ∞ wherever they are not defined and use the relations

$$\begin{aligned}
\Psi^*(U, \Xi) &= \sup\{\, \langle \Xi, V \rangle - \Psi(U, V) \mid V \in \boldsymbol{X} \,\} && \text{(i.e. “ } \mathcal{K}(U) = \mathcal{G}(U)^{-1} \text{ ”)},\\
\Psi(U, V) &= \sup\{\, \langle \Xi, V \rangle - \Psi^*(U, \Xi) \mid \Xi \in \boldsymbol{X}^* \,\} && \text{(i.e. “ } \mathcal{G}(U) = \mathcal{K}(U)^{-1} \text{ ”)}.
\end{aligned}$$

A major advantage of the Onsager form is its flexibility in modeling. Quite often differential equations are written in rate form where the vector field is additively decomposed into different physical phenomena. This additive split can be also used for the Onsager operator, as long as all the different effects are driven by the same functional Φ. Below we will see that $\mathcal{K}$ takes the additive form

$$\mathcal{K} = \mathcal{K}_{\text{diss}} + \mathcal{K}_{\text{diff}} + \mathcal{K}_{\text{react}} + \mathcal{K}_{\text{heat}},$$

such that the evolution equation reads

$$\dot{U} = -\Big(\mathcal{K}_{\text{diss}}\mathrm{D}\Phi + \mathcal{K}_{\text{diff}}\mathrm{D}\Phi + \mathcal{K}_{\text{react}}\mathrm{D}\Phi + \mathcal{K}_{\text{heat}}\mathrm{D}\Phi\Big) = -\mathcal{K}\mathrm{D}\Phi.$$

A similar additive split is not possible for the metric $\mathcal{G}$, as the inverse operator of a sum of operators is difficult to express, in particular if the individual operators $\mathcal{K}_j$ may not be invertible.

2.3 Isothermal and non-isothermal Onsager systems

In applications to thermomechanics we have to distinguish two different cases. In the isothermal case the temperature is assumed to be constant, and the driving functional Φ will be the free energy $\mathcal{F}$. We will start with the non-isothermal case, where the temperature is an independent field that is coupled to the other fields collected into the vector $\boldsymbol{y}$. For such systems we have two functionals, namely the total energy, which is preserved during the evolution of the system, and the total entropy, which acts as a driving force.

In the non-isothermal case the state space $\boldsymbol{X}$ contains states $(\boldsymbol{y}, \theta)$, $(\boldsymbol{y}, e)$, or $(\boldsymbol{y}, s)$, where e is the internal energy density and s the entropy density. In fact, since the physics is independent from our choice of the variable, we follow [Mie11a, Sect. 2.3] and prefer to use an arbitrary scalar variable r, which can be one of the three variables θ, e, s, or another suitable variable for describing the heat distribution. With $\boldsymbol{x} = (\boldsymbol{y}, r)$ we consider

$$\mathcal{E}(\boldsymbol{x}) = \int_\Omega E(x, \boldsymbol{y}(x), \nabla\boldsymbol{y}(x), r(x))\,\mathrm{d}x \text{ and } \mathcal{S}(\boldsymbol{x}) = \int_\Omega S(x, \boldsymbol{y}(x), \nabla\boldsymbol{y}(x), r(x))\,\mathrm{d}x, \quad (2.3)$$

where the constitutive functions E and S are interconnected by the Gibbs relation, which now leads to a definition of the temperature, namely

$$\theta = \Theta(x, \boldsymbol{y}, \nabla\boldsymbol{y}, r) := \frac{\partial_r E(x, \boldsymbol{y}, \nabla\boldsymbol{y}, r)}{\partial_r S(x, \boldsymbol{y}, \nabla\boldsymbol{y}, r)},$$

where we always assume (without loss of generality) that the partial derivatives $\partial_r E$ and $\partial_r S$ are positive.

In the non-isothermal case the total entropy $\mathcal{S}$ (with the physically correct sign) is increasing, so strictly speaking $-\mathcal{S}$ is the driving potential for the gradient flow, but we will not make this distinction in the text, but will always use the corresponding correct signs in the formulas. Our Onsager system $(\boldsymbol{X}, \mathcal{S}, \mathcal{K})$ hence gives rise to the equation $\dot{\boldsymbol{x}} = +\mathcal{K}(\boldsymbol{x})\mathrm{D}\mathcal{S}(\boldsymbol{x})$. To have energy conservation we need

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{E}(\boldsymbol{x}) = \langle \mathrm{D}\mathcal{E}(\boldsymbol{x}), \dot{\boldsymbol{x}}\rangle = \langle \mathcal{E}(\boldsymbol{x}), \mathcal{K}(\boldsymbol{x})\mathrm{D}\mathcal{S}(\boldsymbol{x})\rangle = \langle \mathcal{S}(\boldsymbol{x}), \mathcal{K}(\boldsymbol{x})\mathrm{D}\mathcal{E}(\boldsymbol{x})\rangle \equiv 0,$$

where we used the symmetry $\mathcal{K} = \mathcal{K}^*$ for the last identity. Hence, it is sufficient (but not necessary) to impose the condition

$$\mathcal{K}(\boldsymbol{x})\mathrm{D}\mathcal{E}(\boldsymbol{x}) = 0 \quad \text{for all } \boldsymbol{x} \in \boldsymbol{X}.$$

2.4 Free entropy as driving functional

We also argue that physically relevant driving forces should not depend on the choice of $r \in \{\theta, e, s\}$. Thus, introducing the Helmholtz free energy $\psi = e - \theta s$ and the Helmholtz *free entropy* $\eta = -\psi/\theta = s - e/\theta$ we have the formulas

$$\begin{aligned}\psi &= F(x,Y,r) = E(x,Y,r) - \Theta(x,Y,r)S(x,Y,r) \quad \text{and}\\ \eta &= -\psi/\theta = H(x,Y,r) = S(x,Y,r) - \frac{E(x,Y,r)}{\Theta(x,Y,r)},\end{aligned}$$

where we use the shorthand $Y = (\boldsymbol{y}, \nabla\boldsymbol{y})$. The free entropy η is also called Massieu potential [Massieu 1869] and was in fact introduced before the free energies of Gibbs [1873] and Helmholtz [1882].

At first sight, it seems that there is only a simple difference by a factor $-\theta$, which can be compensated by the Onsager operator (thus turning the dual dissipation potential into a dual entropy production potential, cf. [Mie11a]). However, if gradients $\nabla\boldsymbol{y}$ occur, the driving forces are calculated via variational derivatives involving integrations by parts. Then, it is essential whether an x-dependent factor is inside or outside an integration by parts. In fact, assume $\mathcal{F}(\boldsymbol{y}, r) = \int_\Omega F(x, \boldsymbol{y}, \nabla\boldsymbol{y}, r)\,\mathrm{d}x$ and $\mathcal{H}(\boldsymbol{y}, r) = \int_\Omega H(x, \boldsymbol{y}, \nabla\boldsymbol{y}, r)\,\mathrm{d}x$ with $F = -\Theta H$, then $\mathrm{D}_{\boldsymbol{y}}\mathcal{H}(\boldsymbol{y}, r)$ cannot by replaced by $-\frac{1}{\theta}\mathrm{D}_{\boldsymbol{y}}\mathcal{F}$, since

$$\mathrm{D}_{\boldsymbol{y}}\mathcal{H}(\boldsymbol{y},r) + \tfrac{1}{\theta}\mathrm{D}_{\boldsymbol{y}}\mathcal{F}(\boldsymbol{y},r) = -\operatorname{div}\left(\partial_{\nabla\boldsymbol{y}}H\right) + \frac{1}{\theta}\operatorname{div}(\theta\partial_{\nabla\boldsymbol{y}}H) \;=\; \frac{1}{\theta}\nabla\theta\cdot\partial_{\nabla\boldsymbol{y}}H \;\not\equiv\; 0$$

in general. This difference will be relevant in the Penrose-Fife model discussed in Section 3.1.5. Using the $*$-multiplication of variational derivatives introduced below we have $\mathrm{D}_{\boldsymbol{y}}\mathcal{H}(\boldsymbol{y}, r) = -\frac{1}{\theta} * \mathrm{D}_{\boldsymbol{y}}\mathcal{F}(\boldsymbol{y}, r)$.

In many applications the Onsager operator for non-isothermal systems has a special structure (cf. [Edw98, Ött05, Mie11a]), namely

$$\mathcal{K}(\boldsymbol{y}, r) = \mathcal{M}_{\mathcal{E}} \begin{pmatrix} \mathcal{K}_{\boldsymbol{y}} & 0 \\ 0 & \mathcal{K}_{\text{heat}} \end{pmatrix} \mathcal{M}_{\mathcal{E}}^* \quad \text{with} \tag{2.4a}$$

$$\mathcal{K}_{\text{heat}}\tau = -\operatorname{div}\left(k_{\text{heat}}(\boldsymbol{y}, r)\nabla\tau\right) \quad \text{and} \quad \mathcal{M}_{\mathcal{E}}^* = \begin{pmatrix} I & -(\frac{\square}{\partial_r\mathcal{E}}) * \mathrm{D}_{\boldsymbol{y}}\mathcal{E} \\ 0 & \frac{1}{\partial_r\mathcal{E}} \end{pmatrix}. \tag{2.4b}$$

The "$*$" multiplication is a special operation for variational derivatives. If $\Phi(w) = \int_\Omega F(x, w(x), \nabla w(x))\,\mathrm{d}x$, then for a sufficiently smooth function $\alpha : \Omega \to \mathbb{R}$ we define

$$\alpha * \mathrm{D}_w\Phi(w) := \alpha\,\partial_w F(x, w, \nabla w) - \operatorname{div}\left(\alpha\partial_{\nabla w}F(x, w, \nabla w)\right).$$

The definition of $\mathcal{M}_{\mathcal{E}}$ is such that

$$\mathcal{M}_{\mathcal{E}}^*\mathrm{D}\mathcal{E} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{and} \quad \mathcal{M}_{\mathcal{E}}^*\mathrm{D}\mathcal{S} = \begin{pmatrix} \mathrm{D}_{\boldsymbol{y}}\mathcal{S} - \frac{1}{\Theta} * \mathrm{D}_{\boldsymbol{y}}\mathcal{E} \\ 1/\Theta \end{pmatrix} = \begin{pmatrix} \mathrm{D}_{\boldsymbol{y}}\mathcal{H}(\boldsymbol{y}, r) \\ 1/\Theta \end{pmatrix},$$

where $\mathcal{H}(\boldsymbol{y}, \theta)$ is the total free entropy.

Since $\mathcal{K}_{\text{heat}}1 \equiv 0$, we have the desired relation $\mathcal{K}\mathrm{D}\mathcal{E} \equiv 0$ for energy conservation. Moreover, the coupled system can be rewritten in the form

$$\begin{aligned}\dot{\boldsymbol{y}} &= \mathcal{K}_{\boldsymbol{y}}(\boldsymbol{y}, r)\mathrm{D}_{\boldsymbol{y}}\mathcal{H}(\boldsymbol{y}, r),\\ \dot{r} &= \frac{1}{\partial_r E}\Big(\partial_{\boldsymbol{y}} E \cdot \dot{\boldsymbol{y}} + \partial_{\nabla \boldsymbol{y}} E : \nabla\dot{\boldsymbol{y}} + \mathcal{K}_{\text{heat}}(\boldsymbol{y}, r)\big(1/\Theta(\boldsymbol{y}, \nabla\boldsymbol{y}, r)\big)\Big).\end{aligned}$$

Thus, we conclude that in the non-isothermal case with conserved energy $\mathcal{E}$ the correct driving potential for the non-temperature part $\boldsymbol{y}$ of the system is the free entropy $\mathcal{H}(\boldsymbol{y}, \theta)$.

2.4.1 Isothermal case

The isothermal case is easily derived from the non-isothermal case as follows. We assume that the temperature is constant as the system is embedded into a much larger heat bath, which absorbs or provides heat energy as needed. In this case we can use the above theory with $r = \theta$ and then set $\theta = \theta_*$. In particular we set

$$\mathcal{F}_*(\boldsymbol{y}) := \mathcal{F}(\boldsymbol{y}, \theta_*) = -\theta_* \mathcal{H}(\boldsymbol{y}, \theta_*) \quad \text{and} \quad \mathcal{K}_*(\boldsymbol{y}) = \frac{1}{\theta_*}\mathcal{K}_{\boldsymbol{y}}(\boldsymbol{y}, \theta).$$

Thus, the above Onsager system reduces the triple $(\boldsymbol{Y}, \mathcal{F}_*, \mathcal{K}_*)$. We refer to [Mie11a, Sect. 2.6] for a slightly more elaborate discussion of the isothermal limit in terms of an explicit coupling to a heat bath.

2.5 Principles of thermodynamics

We finally want to comment on the first and second law of TD for the non-isothermal systems discussed above. Our point is that Onsager systems have encoded these principles automatically.

The first law of TD states energy conservation. From our above construction we have immediately obtained that the total energy is conserved. For systems being defined in terms of energy density E depending locally on the fields $\boldsymbol{y}$, $\nabla\boldsymbol{y}$, and r as in (2.3) it is then easy to derive local energy balances, see [Mie11a, Sect. 4].

The second law of TD states that the entropy has to increase. For the total entropy this follows directly from the positive semidefiniteness of $\mathcal{K}$, namely $\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{S}(\boldsymbol{x}) = \langle \mathrm{D}\mathcal{S}(\boldsymbol{x}), \mathcal{K}(\boldsymbol{x})\mathrm{D}\mathcal{S}(\boldsymbol{x})\rangle \geq 0$. For systems being defined in terms of energy density S depending locally on the fields $\boldsymbol{y}$, $\nabla\boldsymbol{y}$, and r as in (2.3) it is then easy to derive local entropy balances with suitable entropy flux and a positive entropy production rate, see [Mie11a, Sect. 4].

However, as the name "Onsager system" suggest, our systems are special dissipative systems fulfilling not only the two fundamental laws but in addition the Onsager principle:

Onsager principle: *rate = sym.pos.semidef. operator × TD conjugate force.*

3 Bulk models for solids

In this section we discuss bulk models where the driving functional and the dissipation potential are given by pure volume integrals. We first collect a few classical parabolic

equations used for modeling solids and recall their gradient structures. Some of these gradient structures are well-known, while in other cases they are only used rarely.

3.1 Five classical systems in gradient form

3.1.1 Allen-Cahn equation

The Allen-Cahn equation is given in terms of the free energy $\mathcal{F}_{\mathrm{AC}}(z) = \int_\Omega \frac{\alpha}{2}|\nabla z|^2 + f(z)\,\mathrm{d}x$ and takes the form

$$\dot z = -k_{\mathrm{AC}}\mathrm{D}\mathcal{F}_{\mathrm{AC}}(z) = -k_{\mathrm{AC}}(-\operatorname{div}\big(\alpha\nabla z\big) + f'(z)).$$

In particular, the dual dissipation potential has the form $\Psi^*(z,\zeta) = \int_\Omega \frac{k_{\mathrm{AC}}}{2}|\zeta|^2\,\mathrm{d}x$, and the Onsager operator is the multiplication operator $\mathcal{K}_{\mathrm{AC}}(z)\zeta = k_{\mathrm{AC}}\zeta$.

3.1.2 Dissipative materials

In general dissipative material models, which are also called *generalized standard materials* (cf. [HaN75, Hac97]), there is a set of internal variables $z : \Omega \to \mathbb{R}^m$ that models microscopic material properties on the macroscopic level. This may include plastic strains, phase transformation, magnetization, polarization, or damage properties, see [Fré02, Mie06]. For simplicity, we neglect here the elastic deformation, which is treated in [Mie11a, Mie11c]. We again consider a free energy of the form

$$\mathcal{F}_{\mathrm{diss}}(z) = \int_\Omega \frac{1}{2}\nabla z{:}\mathbb{A}{:}\nabla z + f(z)\,\mathrm{d}x.$$

Using the Onsager matrix $K_{\mathrm{diss}}(z) \in \mathbb{R}^{m\times m}_{\mathrm{sym}} \geq 0$, the equation takes the form

$$\dot z = -K_{\mathrm{diss}}(z)\mathrm{D}\mathcal{F}_{\mathrm{diss}}(z) = K_{\mathrm{diss}}(z)\Big(\operatorname{div}\big(\mathbb{A}\nabla z\big) - \mathrm{D}f(z)\Big).$$

In plasticity, the evolution equation for z is called flow rule, whereas in ferroelectric materials it is called switching rule. The Onsager relation $\dot z = -K_{\mathrm{diss}}\zeta$ is often generalized to a nonlinear relation in the form $\dot z = \mathrm{D}_\zeta\Psi^*_{\mathrm{diss}}(z,-\zeta)$, where $\zeta = \mathrm{D}\mathcal{F}_{\mathrm{diss}}(z)$ and Ψ^*_{diss} is a non-quadratic dual dissipation potential, e.g. in the form

$$\Psi^*_{\mathrm{diss}}(z,\zeta) = \sigma_{\mathrm{yield}}|\zeta| + \frac{\nu}{q}\|\zeta\|^q.$$

For simplicity, we do not follow this generalization any further here.

3.1.3 Cahn-Hilliard equation

In this case the (vector-valued) internal variable $\varphi : \Omega \to \mathbb{R}^m$ consists of conserved phase indicators with a free energy

$$\mathcal{F}_{\mathrm{CH}}(\varphi) = \int_\Omega \frac{\alpha}{2}|\nabla\varphi|^2 + f(\varphi)\,\mathrm{d}x.$$

The equation is a parabolic system of fourth order given as

$$\dot{\varphi} = -\mathcal{K}_{\mathrm{CH}}(\varphi)\mathrm{D}\mathcal{F}_{\mathrm{CH}}(\varphi) = -\operatorname{div}\Big(\mathbb{M}(\varphi)\nabla\big(-\operatorname{div}(\alpha\nabla\varphi) + \mathrm{D}f(\varphi)\big)\Big).$$

Hence, the Onsager operator $\mathcal{K}_{\mathrm{CH}}$ is a differential operator, namely

$$\mathcal{K}_{\mathrm{CH}}(\varphi)\xi = -\operatorname{div}\big(\mathbb{M}(\varphi)\nabla\xi\big).$$

Note that the evolution leaves the averages $\int_\Omega \varphi(t,x)\,\mathrm{d}x$ constant in time t. This follows from the general property of $\mathcal{K}_{\mathrm{CH}}$ that for $\xi = c \equiv \mathrm{const}$ we have $\mathcal{K}_{\mathrm{CH}}c \equiv 0$.

3.1.4 Heat equation

The heat equation $c(\theta)\dot{\theta} = \operatorname{div}\big(\kappa(\theta)\nabla\theta\big)$ can also be written in Onsager form using the physical entropy as the driving functional, namely $\mathcal{S}(\theta) = \int_\Omega S(\theta(x))\,\mathrm{d}x$. The total energy $\mathcal{E}(\theta) = \int_\Omega E(\theta(x))\,\mathrm{d}x$ has to be conserved along solutions, where $c(\theta) = E'(\theta)$ is the specific heat which satisfies the Gibbs relation $\theta S'(\theta) = E'(\theta)$. We define the Onsager operator

$$\mathcal{K}_{\mathrm{heat}}(\theta)\tau := -\frac{1}{E'(\theta)}\operatorname{div}\Big(k(\theta)\nabla\frac{\tau}{E'(\theta)}\Big),$$

which gives $\mathcal{K}_{\mathrm{heat}}(\theta)\mathrm{D}\mathcal{E}(\theta) \equiv 0$. The Onsager structure yields the equation

$$\begin{aligned}\dot{\theta} = \mathcal{K}_{\mathrm{heat}}(\theta)\mathrm{D}\mathcal{S}(\theta) &= -\frac{1}{E'(\theta)}\operatorname{div}\Big(k(\theta)\nabla\big(S'(\theta)/E'(\theta)\big)\Big)\\ &= -\frac{1}{E'(\theta)}\operatorname{div}\big(k(\theta)\nabla(1/\theta)\big) = \frac{1}{E'(\theta)}\operatorname{div}\Big(\frac{k(\theta)}{\theta^2}\nabla\theta\Big).\end{aligned}$$

Hence, we obtain the original heat equation if we choose $k(\theta) = \theta^2\kappa(\theta)$.

3.1.5 Penrose-Fife model

This model couples the Allen-Cahn equation for an internal variable $z : \Omega \to \mathbb{R}^m$ and the heat equation for the absolute temperature $\theta : \Omega \to]0,\infty[$. Again the energy functional $\mathcal{E}$ is conserved along the solutions, while the entropy functional $\mathcal{S}$ takes the role of the driving functional:

$$\mathcal{E}(z,\theta) = \int_\Omega E(z,\theta)\,\mathrm{d}x \quad \text{and} \quad \mathcal{S}(z,\theta) = \int_\Omega S(z,\theta) - \frac{\alpha}{2}|\nabla z|^2\,\mathrm{d}x..$$

We again assume the Gibbs relation $\partial_\theta E = \theta\partial_\theta S$. Using the mobility matrix $M(z,\theta) \in \mathbb{R}^{m\times m}_{\mathrm{sym}} > 0$ and the heat conduction tensor $\kappa(z,\theta) = k(z,\theta)/\theta^2 \in \mathbb{R}^{d\times d}_{\mathrm{sym}} > 0$ we define the Onsager operator $\mathcal{K}_{\mathrm{PF}} = \mathcal{K}_{\mathrm{AC}} + \mathcal{K}_{\mathrm{heat}}$ with

$$\mathcal{K}_{\mathrm{AC}} = \begin{pmatrix} M & -\frac{1}{\partial_\theta E}M\mathrm{D}_z E\\ -\frac{1}{\partial_\theta E}\mathrm{D}_z E\cdot M & \frac{1}{\partial_\theta E}\mathrm{D}_z E\cdot M\mathrm{D}_z E\end{pmatrix},\ \mathcal{K}_{\mathrm{heat}} = \begin{pmatrix} 0 & 0\\ 0 & -\frac{1}{\partial_\theta E}\operatorname{div}\Big(k\nabla\big(\frac{\square}{\partial_\theta E}\big)\Big)\end{pmatrix}.$$

Here $\mathcal{K}_{\mathrm{PF}}$ has the form (2.4a), where $\mathcal{K}_{\boldsymbol{y}} = M$. Hence, $\mathcal{K}_{\mathrm{PF}}(z,\theta)\mathrm{D}\mathcal{E}(z,\theta) \equiv 0$, which guarantees energy conservation.

Next we claim that the Onsager system $\binom{\dot z}{\dot\theta} = \mathcal{K}_{\rm PF}(z,\theta)\mathrm{D}\mathcal{S}(z,\theta)$ gives exactly the classical Penrose-Fife system [PeF90, PeF93]. The gradient structure was already used, at least implicitly, in [FeS05] and was highlighted explicitly in [Mie11b]. We have

$$\begin{pmatrix}\dot z\\ \dot\theta\end{pmatrix} = \mathcal{K}_{\rm PF}(z,\theta)\begin{pmatrix}\mathrm{D}_z\mathcal{S}\\ \partial_\theta S\end{pmatrix} = \begin{pmatrix} M\big(\mathrm{D}_z S - \alpha\Delta z - \frac{1}{\theta}\mathrm{D}_z E\big)\\ -\frac{1}{\partial_\theta E}\mathrm{D}_z E\cdot M\big(\mathrm{D}_z S - \alpha\Delta z - \frac{1}{\theta}\mathrm{D}_z E\big) - \frac{1}{\partial_\theta E}\operatorname{div}\big(k\nabla\frac{1}{\theta}\big)\end{pmatrix}$$
$$= \begin{pmatrix} M\big(\mathrm{D}_z S - \alpha\Delta z - \frac{1}{\theta}\mathrm{D}_z E\big)\\ -\frac{1}{\partial_\theta E}\mathrm{D}_z E\cdot\dot z + \frac{1}{\partial_\theta E}\operatorname{div}\big(\kappa\nabla\theta\big)\end{pmatrix}$$

Using the free-entropy functional $\mathcal{H}$ defined in Section 2.3 the Penrose-Fife assumes a short and elegant form:

$$\begin{pmatrix}\dot z\\ \dot\theta\end{pmatrix} = \begin{pmatrix} M\mathrm{D}_z\mathcal{H}(z,\theta)\\ -\frac{1}{\partial_\theta E}\mathrm{D}_z E\cdot M\mathrm{D}_z\mathcal{H}(z,\theta) + \frac{1}{\partial_\theta E}\operatorname{div}\big(\kappa\nabla\theta\big)\end{pmatrix},$$

which clearly shows that the free entropy $\mathcal{H}$ drives the motion of the dissipative variable z. In some works the term $M\mathrm{D}_z\mathcal{H}$ is replaced by $-\frac{1}{\theta}M\mathrm{D}_z\mathcal{F}$. We emphasize that this is thermodynamically not correct, since $\mathrm{D}_z\mathcal{H} + \frac{1}{\theta}\mathrm{D}_z\mathcal{F} = -\frac{\alpha}{\theta}\nabla\theta\cdot\nabla z \not\equiv 0$ in general.

3.2 Reaction-diffusion systems

While the above gradient systems are well known, the gradient/Onsager structure for a wider class of reaction-diffusion systems is less known. It was used in a few particular cases (see e.g. [ÖtG97, Yon08, Ede09] and the discussion in Section 3.2.2) but only highlighted in its own right in [Mie11b]. The central point is that in the Onsager form we have an additive splitting of the Onsager operator into a diffusive part and a reaction part, namely $\dot{\boldsymbol{u}} = -\big(\mathcal{K}_{\rm diff}(\boldsymbol{u}) + \mathcal{K}_{\rm react}(\boldsymbol{u})\big)\mathcal{F}_{\rm chem}(\boldsymbol{u})$, where $\boldsymbol{u}:\Omega\to]0,\infty[^I$ is the vector of densities of the species $X_1,...,X_I$. The free-energy functional $\mathcal{F}_{\rm chem}$, which is also called the relative entropy with respect to the reference density $\boldsymbol{u}^*$, takes the form

$$\mathcal{F}_{\rm chem}(\boldsymbol{u}) = \int_\Omega \sum_{i=1}^I u_i^*\lambda(u_i(x)/u_i^*)\,\mathrm{d}x \quad \text{where} \quad \lambda(\nu) = \nu(\log\nu - 1). \tag{3.1}$$

3.2.1 Diffusion systems

For the gradient structure of diffusion systems $\dot{\boldsymbol{u}} = \operatorname{div}\big(\mathbb{M}(\boldsymbol{u})\nabla\boldsymbol{u}\big)$ one might be tempted to use a functional involving the gradient ∇u, however we have to use the relative entropy as a driving functional, because we have to use the same functional for modeling the reactions. Hence, we use the Wasserstein approach to diffusion introduced by Otto in [JKO98, Ott01].

The diffusion system will take the form $\dot{\boldsymbol{u}} = -\mathcal{K}_{\rm diff}(\boldsymbol{u})\mathrm{D}\mathcal{F}(u)$ with an Onsager operator $\mathcal{K}_{\rm diff}$ given via

$$\mathcal{K}_{\rm diff}(\boldsymbol{u})\boldsymbol{\mu} = -\operatorname{div}\big(\widetilde{\mathbb{M}}(\boldsymbol{u})\nabla\boldsymbol{\mu}\big),$$

where $\widetilde{\mathbb{M}}(\boldsymbol{u}):\mathbb{R}^{m\times d}\to\mathbb{R}^{m\times d}$ is a symmetric and positive semi-definite tensor of order 4. The Onsager operator can also be implicitly defined via the dual dissipation potential,

which will be useful later:

$$\Psi^*_{\text{Wass}}(\boldsymbol{u},\boldsymbol{\mu}) = \int_\Omega \frac{1}{2}\nabla\boldsymbol{\mu}{:}\widetilde{\mathbb{M}}(\boldsymbol{u}){:}\nabla\boldsymbol{\mu}\,\mathrm{d}x,$$

where $\boldsymbol{\mu} = (\mu_i)_{i=1,..,I}$ is the vector of chemical potentials, which occurs as the driving force

$$\boldsymbol{\mu} = \mathrm{D}_{\boldsymbol{u}}\mathcal{F}_{\text{chem}}(\boldsymbol{u}) = \mathbf{log}\,\boldsymbol{u} - \mathbf{log}\,\boldsymbol{u}^*.$$

Hence, if the reference densities $\boldsymbol{\mu}^*$ are spatially constant (which is usually not true in heterostructures like semiconductors) the Onsager system leads to the diffusion system

$$\dot{\boldsymbol{u}} = \operatorname{div}\big(\widetilde{\mathbb{M}}(\boldsymbol{u})\nabla(\mathbf{log}\,\boldsymbol{u} - \mathbf{log}\,\boldsymbol{u}^*)\big) = \operatorname{div}\big(\mathbb{M}(\boldsymbol{u})\nabla\boldsymbol{u}\big), \quad \text{where } \widetilde{\mathbb{M}}(\boldsymbol{u}) = \mathbb{M}(u)\operatorname{diag}(\boldsymbol{u}).$$

We emphasize that $\widetilde{\mathbb{M}}$ has to be symmetric by Onsager's symmetry relations, which leads to unsymmetric operators $\mathbb{M}$, if there is cross-diffusion. E.g. assuming $I = 2$, $\boldsymbol{u}^* = (1,1)$, and isotropy, we arrive at the coupled system

$$\begin{pmatrix}\dot{u}_1\\ \dot{u}_2\end{pmatrix} = \begin{pmatrix}\operatorname{div}\big(\frac{\widetilde{m}_1(u_1,u_2)}{u_1}\nabla u_1 + \frac{\widetilde{m}_{12}(u_1,u_2)}{u_2}\nabla u_2\big)\\ \operatorname{div}\big(\frac{\widetilde{m}_{12}(u_1,u_2)}{u_1}\nabla u_1 + \frac{\widetilde{m}_2(u_1,u_2)}{u_2}\nabla u_2\big)\end{pmatrix},$$

where $\widetilde{m}_1,\ \widetilde{m}_2 > 0$ and $\widetilde{m}_1\widetilde{m}_2 - \widetilde{m}_{12}^2 \geq 0$. Hence, $\widetilde{m}_{12} \neq 0$ means cross-diffusion and yields the unsymmetry of $\mathbb{M}$.

3.2.2 Chemical reaction kinetics

Chemical reaction systems are ODE systems $\dot{\boldsymbol{u}} = \boldsymbol{R}(\boldsymbol{u})$, where often the right-hand side is written in terms of polynomials associated to the reaction kinetics. It was observed in [Mie11b] that under the assumption of detailed balance (also called reversibility) such systems have a gradient structure with the relative entropy as the driving functional.

We assume that there are R reactions of mass-action type (cf. e.g. [DeM84, GiM04, KjB08]) between the species $X_1, ..., X_I$ denoted by

$$\alpha_1^r X_1 + \cdots + \alpha_I^r X_I \underset{k_r^{\text{bw}}}{\overset{k_r^{\text{fw}}}{\rightleftharpoons}} \beta_1^r X_1 + \cdots + \beta_I^r X_I,$$

where k_r^{bw} and k_r^{fw} are the backward and forward reaction rates, and the vectors $\boldsymbol{\alpha}^r,\ \boldsymbol{\beta}^r \in \mathbb{N}_0^I$ contain the stoichiometric coefficients. For the chemical reaction $2\,\mathrm{CO} + 1\,\mathrm{O}_2 \rightleftharpoons 2\,\mathrm{CO}_2$ we have $\boldsymbol{\alpha} = (2,1,0)^\mathsf{T}$ and $\boldsymbol{\beta} = (0,0,2)^\mathsf{T}$.

The associated reaction system for the densities (in a spatially homogeneous system, where diffusion can be neglected) reads

$$\dot{\boldsymbol{u}} = \boldsymbol{R}(\boldsymbol{u}) := -\sum_{r=1}^{R}\big(k_r^{\text{fw}}\boldsymbol{u}^{\boldsymbol{\alpha}^r} - k_r^{\text{bw}}\boldsymbol{u}^{\boldsymbol{\beta}^r}\big)\Big(\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r\Big), \tag{3.2}$$

where we use the monomial notation $\boldsymbol{u}^{\boldsymbol{\alpha}} = u_1^{\alpha_1}\cdots u_I^{\alpha_I}$.

The main assumption to obtain a gradient structure is that of *detailed balance*, which means that there exists a reference density vector $\boldsymbol{u}^*$ such that all R reactions are balanced individually, namely

$$\exists\, \boldsymbol{u}_* \in]0,\infty[^I \;\; \forall\, r = 1, ..., R \;\forall\, \boldsymbol{u} \in]0,\infty[^I : \;\; k_r^{\mathrm{fw}}(\boldsymbol{u})\boldsymbol{u}_*^{\boldsymbol{\alpha}^r} = k_r^{\mathrm{bw}}(\boldsymbol{u})\boldsymbol{u}_*^{\boldsymbol{\beta}^r} =: k_r^*(\boldsymbol{u}). \tag{3.3}$$

Here we have used the freedom to allow for reaction coefficients depending on the densities (and later also on other material properties like temperature).

As in [Mie11b] we now define the Onsager matrix

$$\mathbb{H}(\boldsymbol{u}) = \sum_{r=1}^{R} k_r^*(\boldsymbol{u}) \Lambda\big(\tfrac{\boldsymbol{u}^{\boldsymbol{\alpha}^r}}{\boldsymbol{u}_*^{\boldsymbol{\alpha}^r}}, \tfrac{\boldsymbol{u}^{\boldsymbol{\beta}^r}}{\boldsymbol{u}_*^{\boldsymbol{\beta}^r}}\big) \big(\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r\big) \otimes \big(\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r\big) \text{ with } \Lambda(a,b) = \frac{a-b}{\log a - \log b} \tag{3.4}$$

and find that the reaction system (3.2) takes the form

$$\dot{\boldsymbol{u}} = \boldsymbol{R}(\boldsymbol{u}) = -\mathbb{H}(\boldsymbol{u}) \mathrm{D}\mathcal{F}_{\mathrm{chem}}(\boldsymbol{u}). \tag{3.5}$$

This follows easily by using the definition of Λ and the rules for logarithms, namely

$$\big(\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r\big) \cdot \big(\boldsymbol{\mu} - \boldsymbol{\mu}^*\big) = \log\big(\boldsymbol{u}^{\boldsymbol{\alpha}^r} / \boldsymbol{u}_*^{\boldsymbol{\alpha}^r}\big) - \log\big(\boldsymbol{u}^{\boldsymbol{\beta}^r} / \boldsymbol{u}_*^{\boldsymbol{\beta}^r}\big).$$

The quotient $\Lambda(a,b) = \frac{a-b}{\log a - \log b}$ (or variants of it) have occurred occasionally in the modeling of reaction kinetics: In [ÖtG97, Eqn. (113)] the reaction $\mathrm{N_2 + 3H_2 \rightleftharpoons 2NH_3}$ is written in GENERIC, which includes the gradient structure for the reaction. In [Ede09, Def. 3.22] the mapping $(\mu, \eta) \mapsto 1/\Lambda(\mathrm{e}^{\mu}, \mathrm{e}^{\eta})$ is called the *ideal resistance function*. In [Yon08, Sect. VII] the definition of Δ_j contains $\int_0^1 \mathrm{e}^{\sigma a_j}\, \mathrm{d}\sigma = (\mathrm{e}^{a_j} - 1)/a_j = \Lambda(\mathrm{e}^{a_j}, 1)$ to show that the reaction terms have the Onsager structure displayed in (3.5).

3.2.3 Coupling diffusion and reaction

We summarize the previous two subsections by stating the following general result from [Mie11b] for Onsager structures for reaction-diffusion system.

Theorem 3.1 *If the reaction diffusion system* $\dot{\boldsymbol{u}} = \mathrm{div}\big(\mathbb{M}(\boldsymbol{u})\nabla \boldsymbol{u}\big) + \boldsymbol{R}(\boldsymbol{u})$ *with* $\boldsymbol{R}(\boldsymbol{u}) = -\sum_{r=1}^{R} \big(k_r^{fw}(\boldsymbol{u})\boldsymbol{u}^{\boldsymbol{\alpha}^r} - k_r^{bw}(\boldsymbol{u})\boldsymbol{u}^{\boldsymbol{\beta}^r}\big)\big(\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r\big)$ *satisfies the detailed balance condition* (3.3) *and if* $\widetilde{\mathbb{M}}(\boldsymbol{u}) = \mathbb{M}(\boldsymbol{u})\mathrm{diag}(\boldsymbol{u})$ *is symmetric and positive semidefinite, then it is an Onsager system* $\dot{\boldsymbol{u}} = -\mathcal{K}_{\mathrm{RD}}(\boldsymbol{u})\mathrm{D}\mathcal{F}_{\mathrm{chem}}$ *with*

$$\mathcal{F}_{\mathrm{chem}}(\boldsymbol{u}) = \int_\Omega \sum_{i=1}^{I} u_i^* \lambda(u_i(x)/u_i^*)\, \mathrm{d}x, \;\; \boldsymbol{\Psi}_{\mathrm{RD}}^*(\boldsymbol{u}, \boldsymbol{\mu}) = \frac{1}{2}\int_\Omega \nabla\boldsymbol{\mu} : \widetilde{\mathbb{M}}(\boldsymbol{u}) : \nabla\boldsymbol{\mu} + \boldsymbol{\mu} \cdot \mathbb{H}(\boldsymbol{u}) \cdot \boldsymbol{\mu}\, \mathrm{d}x.$$

We mention that many reaction-diffusion systems studied in the literature (including semiconductor models involving an elliptic equation for the electrostatic potential), see e.g. [GlH05, DeF06, DeF07, Gli09, BoP11], have the structure developed above. So far, the gradient structure was not used explicitly, only the Liapunov property of the free energy $\mathcal{F}_{\mathrm{chem}}$ was exploited for deriving a priori estimates.

3.3 Consistent isothermal coupling to general bulk systems

We first discuss the isothermal case, where the driving functional is the free energy. Using the above Onsager structures for the internal variables z (non-conserved) and φ (conserved) and the chemical densities $\boldsymbol{u}$ we are now able to write consistent bulk systems by simply adding the free energies and the dual dissipation functionals:

$$\begin{aligned}\mathcal{F}(z,\varphi,\boldsymbol{u}) &= \mathcal{F}_{\text{diss}}(z)+\mathcal{F}_{\text{CH}}(\varphi)+\mathcal{F}_{\text{RD}}(\boldsymbol{u})+\mathcal{F}_{\text{coupl}}(z,\varphi,\boldsymbol{u}),\\ \Psi^*(z,\varphi,\boldsymbol{u};\zeta,\xi,\boldsymbol{\mu}) &= \Psi^*_{\text{diss}}(z;\zeta)+\Psi^*_{\text{CH}}(\varphi;\xi)+\Psi^*_{\text{RD}}(\boldsymbol{u};\boldsymbol{\mu})+\Psi^*_{\text{coupl}}(z,\varphi,\boldsymbol{u};\zeta,\xi,\boldsymbol{\mu}).\end{aligned}$$

Neglecting the coupling term Ψ^*_{coupl} in the dual dissipation potential we are led to

$$\begin{pmatrix}\dot z\\ \dot\varphi\\ \dot{\boldsymbol{u}}\end{pmatrix} = -\begin{pmatrix}\mathcal{K}_{\text{diss}}(z) & 0 & 0\\ 0 & \mathcal{K}_{\text{CH}}(\varphi) & 0\\ 0 & 0 & \mathcal{K}_{\text{RD}}(\boldsymbol{u})\end{pmatrix}\begin{pmatrix}\mathrm{D}\mathcal{F}_{\text{diss}}(z)+\mathrm{D}_z\mathcal{F}_{\text{coupl}}(z,\varphi,\boldsymbol{u})\\ \mathrm{D}\mathcal{F}_{\text{CH}}(\varphi)+\mathrm{D}_\varphi\mathcal{F}_{\text{coupl}}(z,\varphi,\boldsymbol{u})\\ \mathrm{D}\mathcal{F}_{\text{chem}}(\boldsymbol{u})+\mathrm{D}_{\boldsymbol{u}}\mathcal{F}_{\text{coupl}}(z,\varphi,\boldsymbol{u})\end{pmatrix}. \tag{3.6}$$

Of course, the Onsager operator $\mathcal{K}$ may be much more general than indicated here. Staying in the diagonal form of (3.6) we may allow that each of the diagonal entries $\mathcal{K}_{\text{diss}}$, $\mathcal{K}_{\text{CH}}$, and $\mathcal{K}_{\text{RD}}$ may depend on $(z,\varphi,\boldsymbol{u})$. Moreover, we may introduce off-diagonal terms through Ψ^*_{coupl}.

For the full generality, one should not think about adding three terms with a small coupling. One should rather take one free energy like

$$\mathcal{F}(z,\varphi,\boldsymbol{u})=\int_\Omega F(x,z(x),\varphi(x),\boldsymbol{u}(x))+\frac{\gamma}{2}|\nabla z(x)|^2+\frac{\delta}{2}|\nabla\varphi(x)|^2\,\mathrm{d}x.$$

In particular, we may consider the case where the reference density vector $\boldsymbol{u}^*$ in the detailed-balance condition (3.3) depends on (z,φ). As an example consider the case without conserved phase-field variables and $\boldsymbol{u}=(u_1,u_2)$ and let

$$\mathcal{F}(z,\boldsymbol{u})=\int_\Omega f(z)+\frac{\gamma}{2}|\nabla z|^2+w_1(z)\lambda\big(u_1/w_1(z)\big)+w_2(z)\lambda\big(u_2/w_2(z)\big)\,\mathrm{d}x,$$

where the functions $w_j : z\mapsto w_j(z)>0$ are given and $\lambda(\nu)=\nu(\log\nu-1)$ as above. Together with the dual dissipation potential

$$\begin{aligned}\Psi^*(z,\boldsymbol{u};\zeta,\boldsymbol{\mu})=\frac12\int_\Omega &\zeta\cdot k_{\text{AC}}(z,\boldsymbol{u})\zeta+m_1(z,\boldsymbol{u})|\nabla\mu_1|^2+m_2(z,\boldsymbol{u})|\nabla\mu_2|^2\\ &+k_{\text{react}}(z,\boldsymbol{u})\big((\boldsymbol{\alpha}-\boldsymbol{\beta})\cdot\boldsymbol{\mu}\big)^2\,\mathrm{d}x\end{aligned}$$

we find the following coupled system:

$$\begin{aligned}\dot z &= k_{\text{AC}}(z,\boldsymbol{u})\Big(\operatorname{div}\big(\gamma\nabla z\big)-f'(z)+\frac{u_1}{w_1(z)}\mathrm{D}_z w_1(z)+\frac{u_2}{w_2(z)}\mathrm{D}_z w_2(z)\Big),\\ \begin{pmatrix}\dot u_1\\ \dot u_2\end{pmatrix} &= \begin{pmatrix}\operatorname{div}\big(m_1(z,\boldsymbol{u})\nabla(\log u_1-\log w_1(z))\big)\\ \operatorname{div}\big(m_2(z,\boldsymbol{u})\nabla(\log u_2-\log w_2(z))\big)\end{pmatrix}\\ &\quad -k_{\text{react}}(z,\boldsymbol{u})\Lambda\big(\tfrac{\boldsymbol{u}^{\boldsymbol{\alpha}}}{\boldsymbol{w}(z)^{\boldsymbol{\alpha}}},\tfrac{\boldsymbol{u}^{\boldsymbol{\beta}}}{\boldsymbol{w}(z)^{\boldsymbol{\beta}}}\big)(\boldsymbol{\alpha}-\boldsymbol{\beta})\otimes(\boldsymbol{\alpha}-\boldsymbol{\beta})\cdot(\log\boldsymbol{u}-\log\boldsymbol{w}(z)).\end{aligned}$$

Using the functions $W_j(z) = \log w_j(z)$ and employing the definition of Λ we can reformulate the system in the form

$$\begin{aligned}\dot z \quad &= k_{\mathrm{AC}}(z,\boldsymbol{u})\Big(\operatorname{div}\big(\gamma\nabla z\big) - f'(z) + u_1\mathrm{D}_z W_1(z) + u_2\mathrm{D}_z W_2(z)\Big),\\ \begin{pmatrix}\dot u_1\\ \dot u_2\end{pmatrix} &= \begin{pmatrix}\operatorname{div}\big(\frac{m_1(z,\boldsymbol{u})}{u_1}\nabla u_1 - m_1(z,\boldsymbol{u})\mathrm{D}_z W_1(z)\nabla z\big)\\ \operatorname{div}\big(\frac{m_2(z,\boldsymbol{u})}{u_2}\nabla u_2 - m_2(z,\boldsymbol{u})\mathrm{D}W_2(z)\nabla z\big)\end{pmatrix}\\ &\quad - k_{\mathrm{react}}(z,\boldsymbol{u})\big(\boldsymbol{u}^{\boldsymbol{\alpha}}\mathrm{e}^{-\boldsymbol{\alpha}\cdot\boldsymbol{W}(z)} - \boldsymbol{u}^{\boldsymbol{\beta}}\mathrm{e}^{-\boldsymbol{\beta}\cdot\boldsymbol{W}(z)}\big)(\boldsymbol{\alpha}-\boldsymbol{\beta}).\end{aligned}$$

Thus, even without assuming any coupling inside the Onsager structure, we still obtain a kind of cross-diffusion arising from the z-dependence of the reference densities $w_j(z)$.

3.4 Non-isothermal coupled systems

We now add to the variables $\boldsymbol{y} := (z, \varphi, \boldsymbol{u})$ the absolute temperature $\theta > 0$ and use Onsager operators in the form (2.4), following the derivation of Section 2.3, where now

$$\mathcal{K}_{\boldsymbol{y}}(\boldsymbol{y}) = \begin{pmatrix}\mathcal{K}_{\mathrm{diss}} & & \\ & \mathcal{K}_{\mathrm{CH}} & \\ & & \mathcal{K}_{\mathrm{RD}}\end{pmatrix}.$$

As in the Penrose-Fife model (cf. Section 3.1.5) we again treat a closed systems in which the total energy $\mathcal{E}$ is conserved while the total entropy increases and serves as a driving functional. Now the Onsager operator $\mathcal{K}$ is given in terms of an entropy-production potential

$$\Psi^*(\boldsymbol{y},\theta;\boldsymbol{\eta},\tau) = \frac{1}{2}\Big\langle \binom{\boldsymbol{\eta}}{\tau}, \mathcal{K}(\boldsymbol{y},\theta)\binom{\boldsymbol{\eta}}{\tau}\Big\rangle.$$

3.4.1 Reaction-diffusion systems with temperature

We now restrict to a system described by $(\boldsymbol{u},\theta)$ with functionals

$$\mathcal{E}(\boldsymbol{u},\theta) = \int_\Omega E(x,\boldsymbol{u}(x),\theta(x))\,\mathrm{d}x \quad \text{and} \quad \mathcal{S}(\boldsymbol{u},\theta) = \int_\Omega S(x,\boldsymbol{u}(x),\theta(x))\,\mathrm{d}x,$$

where the integrands are strictly local, i.e. they do not depend on $\nabla\boldsymbol{u}$ and $\nabla\theta$. As throughout the paper, the densities may explicitly depend on the material point, but we will omit this dependence in the sequel. The energy density E and the entropy density S satisfy the Gibbs relation $\partial_\theta E = \theta\partial_\theta S$ and the positivity of the specific heat $\partial_\theta E > 0$.

The dual entropy-production potential Ψ^* will depend on the state $(\boldsymbol{u},\theta)$ and the thermodynamically conjugate variables $(\boldsymbol{\mu},\tau)$. In principle, Ψ^* will contain three parts, namely a diffusion, a reaction, and a heat conduction part. However, the heat conduction and the diffusion can be joined into one quadratic form on $(\nabla\boldsymbol{\mu},\nabla\tau)$, thus allowing for "cross-diffusion" effects between chemical diffusion and heat transfer, which is needed to model thermophilic or thermophobic reactions occurring e.g. in polymers, see [AWR12].

To guarantee energy conservation, we mimic the definition of $\mathcal{M}_{\mathcal{E}}$ in (2.4b) (see also [Mie11b, Sect. 3.6]) and consider

$$\Psi^*(\boldsymbol{u},\theta;\boldsymbol{\mu},\tau) = \widetilde{\Psi}^*(\boldsymbol{u},\theta;\boldsymbol{\mu}-\tfrac{\tau}{\partial_\theta E}\partial_{\boldsymbol{u}}E,\tfrac{\tau}{\partial_\theta E}) \tag{3.7a}$$

$$\text{with } \widetilde{\Psi}^*(\boldsymbol{u},\theta;\widetilde{\boldsymbol{\mu}},\widetilde{\tau}) = \frac{1}{2}\int_\Omega (\nabla\widetilde{\boldsymbol{\mu}},\nabla\widetilde{\tau}) : \mathbb{M}(\boldsymbol{u},\theta)(\nabla\widetilde{\boldsymbol{\mu}},\nabla\widetilde{\tau}) + \widetilde{\boldsymbol{\mu}}\cdot\mathbb{H}(\boldsymbol{u},\theta)\widetilde{\boldsymbol{\mu}}\,\mathrm{d}x, \tag{3.7b}$$

where $\mathbb{H}$ is given as in (3.4). The mobility tensor $\mathbb{M}(\boldsymbol{u},\theta) : \mathbb{R}^{I\times d}\times\mathbb{R}^d \to \mathbb{R}^{I\times d}\times\mathbb{R}^d$ is symmetric and positive semidefinite and has the block structure

$$\mathbb{M}(\boldsymbol{u},\theta) = \begin{pmatrix} \mathbb{M}_{\boldsymbol{uu}}(\boldsymbol{u},\theta) & \mathbb{M}_{\boldsymbol{u}\theta}(\boldsymbol{u},\theta) \\ \mathbb{M}^*_{\boldsymbol{u}\theta}(\boldsymbol{u},\theta) & \mathbb{M}_{\theta\theta}(\boldsymbol{u},\theta) \end{pmatrix}.$$

The construction of Ψ^* is such that $\Psi^*(\boldsymbol{u},\theta;\boldsymbol{\mu},\tau) = \Psi^*(\boldsymbol{u},\theta;(\boldsymbol{\mu},\tau)+\lambda\mathrm{D}\mathcal{E}(\boldsymbol{u},\theta))$ for all $\lambda\in\mathbb{R}$. Hence, the associated Onsager operator $\mathcal{K}$ satisfies $\mathcal{K}\mathrm{D}\mathcal{E}\equiv 0$. Moreover, we see that Ψ^* only depends on

$$\mathrm{D}_{\boldsymbol{u}}\mathcal{S} - \frac{1}{\theta}\mathrm{D}_{\boldsymbol{u}}\mathcal{E} = \partial_{\boldsymbol{u}}S - \frac{1}{\theta}\partial_{\boldsymbol{u}}E = \partial_{\boldsymbol{u}}H \quad\text{and}\quad \frac{\partial_\theta S}{\partial_\theta E} = \frac{1}{\theta},$$

where $H = -\psi/\theta = S - E/\theta$ is the free entropy.

The Onsager system $\frac{\mathrm{d}}{\mathrm{d}t}\binom{\boldsymbol{u}}{\theta} = \mathcal{K}\mathrm{D}\mathcal{S}$ for the evolution of $(\boldsymbol{u},\theta)$ is the coupled PDE

$$\begin{aligned}
\dot{\boldsymbol{u}} &= -\operatorname{div}\boldsymbol{j}_{\boldsymbol{u}} + \mathbb{H}(\boldsymbol{u},\theta)\big(\partial_{\boldsymbol{u}}S(\boldsymbol{u},\theta) - \tfrac{1}{\theta}\partial_{\boldsymbol{u}}E(\boldsymbol{u},\theta)\big),\\
\dot\theta &= -\tfrac{1}{\partial_\theta E}\operatorname{div}\boldsymbol{j}_\theta + \tfrac{1}{\partial_\theta E}\partial_{\boldsymbol{u}}E\cdot\big(\operatorname{div}\boldsymbol{j}_{\boldsymbol{u}} - \mathbb{H}(\boldsymbol{u},\theta)\big(\partial_{\boldsymbol{u}}S(\boldsymbol{u},\theta) - \tfrac{1}{\theta}\partial_{\boldsymbol{u}}E(\boldsymbol{u},\theta)\big),
\end{aligned}$$

where $\boldsymbol{j}_{\boldsymbol{u}} = \mathbb{M}_{\boldsymbol{uu}}(\boldsymbol{u},\theta)\nabla\big(\partial_{\boldsymbol{u}}S(\boldsymbol{u},\theta) - \frac{1}{\theta}\partial_{\boldsymbol{u}}E(\boldsymbol{u},\theta)\big) + \mathbb{M}_{\boldsymbol{u}\theta}(\boldsymbol{u},\theta)\nabla(1/\theta)\big)$ and $\boldsymbol{j}_\theta = \mathbb{M}^*_{\boldsymbol{u}\theta}(\boldsymbol{u},\theta)\nabla\big(\partial_{\boldsymbol{u}}S(\boldsymbol{u},\theta) - \frac{1}{\theta}\partial_{\boldsymbol{u}}E(\boldsymbol{u},\theta)\big) + \mathbb{M}_{\theta\theta}(\boldsymbol{u},\theta)\nabla(1/\theta)\Big)$. In the simplest isotropic case one chooses $\mathbb{M}_{\boldsymbol{uu}}(\boldsymbol{u},\theta)\nabla\boldsymbol{\mu} = (m_i u_i\nabla\mu_i)_{j=1,\dots,I}$, $\mathbb{M}_{\boldsymbol{u}\theta}=0$, and $\mathbb{M}_{\theta\theta}(\boldsymbol{u},\theta) = \theta^2\kappa$.

We refer to [GiM04, Sect. 2.5] and [Yon08, Sect. VII] for useful representations of $s = \overline{S}(\boldsymbol{u},\theta)$, $e = \overline{E}(\boldsymbol{u},\theta)$, and $\boldsymbol{u}^* = \overline{\boldsymbol{w}}(\theta)$.

3.4.2 Reaction-diffusion systems with internal energy

A major advantage of gradient and Onsager systems is that it is very easy to change coordinates. For energy-preserving non-isothermal reaction-diffusion systems it is often easier to formulate the theory in terms of the density vector $\boldsymbol{u}:\Omega\to]0,\infty[^I$ and the internal energy $e:\Omega\to\mathbb{R}$. Thus, the functionals are

$$\widehat{\mathcal{E}}(\boldsymbol{u},u) = \int_\Omega e(x)\,\mathrm{d}x \quad\text{and}\quad \widehat{\mathcal{S}}(\boldsymbol{u},e) = \int_\Omega \widehat{S}(x,\boldsymbol{u}(x),e(x))\mathrm{d}x.$$

Now the Gibbs relation leads to the definition of temperature as $\theta = \Theta(\boldsymbol{u},e) := 1/\partial_e S(\boldsymbol{u},e)$, where the relation $\partial_e\widehat{S}(\boldsymbol{u},e) > 0$ is imposed.

The major advantage of the formulation in terms of $(\boldsymbol{u},e)$ is that energy conservation is a linear constraint. Moreover, following [AGH02] it is reasonable to assume that $\widehat{S}$ is

a concave function in $(\boldsymbol{u}, e)$. Finally, the driving force through the free entropy is most simple, as $\partial_{\boldsymbol{u}} H = \partial_{\boldsymbol{u}} \widehat{S}$, since using $\widehat{E}(\boldsymbol{u}, e) := e$ we have $\partial_{\boldsymbol{u}} \widehat{E} \equiv 0$, cf. [Mie11a, Sect. 2.3].

Thus, the equations in Section 3.4.1 can be equivalently written in $(\boldsymbol{u}, e)$ using the dual entropy-production potential

$$\widehat{\Psi}^*(\boldsymbol{u}, e; \boldsymbol{\mu}, \varepsilon) = \frac{1}{2} \int_\Omega (\nabla \boldsymbol{\mu}, \nabla \varepsilon) : \widehat{\mathbb{M}}(\boldsymbol{u}, e)(\nabla \boldsymbol{\mu}, \nabla \varepsilon) + \boldsymbol{\mu} \cdot \widehat{\mathbb{H}}(\boldsymbol{u}, e) \boldsymbol{\mu} \, \mathrm{d}x,$$

where $\widehat{\mathbb{M}}$ and $\widehat{\mathbb{H}}$ are obtained from $\mathbb{M}$ and $\mathbb{H}$, respectively, by substituting $\theta = \widehat{\Theta}(\boldsymbol{u}, e)$. As a consequence of the simple form of $\widehat{\mathcal{E}}$, and hence of $\widehat{\Psi}^*$, the evolution equations for $(\boldsymbol{u}, e)$ take the simpler form

$$\begin{aligned}
\dot{\boldsymbol{u}} &= -\operatorname{div}\Big(\widehat{\mathbb{M}}_{\boldsymbol{u}\boldsymbol{u}}(\boldsymbol{u}, e) \nabla\big(\partial_{\boldsymbol{u}} \widehat{S}(\boldsymbol{u}, e)\big) + \widehat{\mathbb{M}}_{\boldsymbol{u}e}(\boldsymbol{u}, e) \nabla\big(\partial_e \widehat{S}(\boldsymbol{u}, e)\big) \Big) + \widehat{\mathbb{H}}(\boldsymbol{u}, e) \partial_{\boldsymbol{u}} S(\boldsymbol{u}, e), \\
\dot{e} &= -\operatorname{div}\Big(\widehat{\mathbb{M}}^*_{\boldsymbol{u}e}(\boldsymbol{u}, e) \nabla\big(\partial_{\boldsymbol{u}} S(\boldsymbol{u}, e)\big) + \widehat{\mathbb{M}}_{ee}(\boldsymbol{u}, e) \nabla\big(\partial_e \widehat{S}(\boldsymbol{u}, e)\big) \Big).
\end{aligned}$$

This form has the major advantage that we can read of "parabolicity" in the sense of Petrovsky (cf. [LSU68, Sect. VII.8]) for the full coupled system by assuming that $\widehat{\mathbb{M}}$ is positive definite and that $\mathrm{D}^2 S$ is negative definite. Hence, local existence results can be obtained from [Ama93].

Moreover, we are able to postulate suitable strongly coupled models by assuming that $\widehat{S}$ has the form

$$\widehat{S}(\boldsymbol{u}, e) = s(e) - \boldsymbol{u} \cdot \big(\log \boldsymbol{u} - \log \boldsymbol{w}(e) \big), \tag{3.8}$$

where $\boldsymbol{u}^* = \boldsymbol{w}(e)$ are now the reference densities in the detailed balance condition (3.3), which may now depend on the internal energy (i.e. on the temperature). The concavity can be checked by using

$$-\binom{\boldsymbol{\mu}}{\varepsilon} \cdot \mathrm{D}^2 \widehat{S}(\boldsymbol{u}, e) \binom{\boldsymbol{\mu}}{\varepsilon} = \textstyle\sum_{i=1}^I u_i \big(\frac{\mu_i}{u_i} - \varepsilon \frac{w_i'(e)}{w_i(e)} \big)^2 + \varepsilon^2 \big(-s''(e) - \sum_{i=1}^I u_i \frac{w_i''(e)}{w_i(e)} \big).$$

Thus, we have strict convexity on the whole domain $]0, \infty[^I \times]e_0, \infty[$ if and only if $s''(e) < 0$ and $w_i''(e) \le 0$ for all i. Hence, good choices for $s(e)$ and $\boldsymbol{w}(e)$ are given in the form

$$\begin{aligned}
&s(e) = c \log e \text{ or } s(e) = c\, e^\sigma \text{ with } c > 0 \text{ and } \sigma \in]0, 1[, \\
&w_i(e) = a_i e^{b_i} \quad \text{for some } a_i > 0 \text{ and } b_i \in [0, 1].
\end{aligned} \tag{3.9}$$

In the case $s(e) = c \log e$ we find the simple relation $1/\theta = \partial_e \widehat{S}(\boldsymbol{u}, e) = \big(c + \boldsymbol{b} \cdot \boldsymbol{u}\big)/e$, where $\boldsymbol{b} = (b_i)_{i=1,\dots,I}$. Hence, we obtain the simple linear relation $e = \overline{E}(\boldsymbol{u}, \theta) = \big(c + \boldsymbol{b} \cdot \boldsymbol{u}\big)\, \theta$.

4 Bulk-interface interaction

4.1 General setup for interfaces

We now consider a domain Ω containing an interface Γ separating Ω into an upper part Ω_+ and a lower part Ω_-, i.e. Ω is the disjoint union of Ω_+, Γ, and Ω_-. For later convenience we denote that part of the surface of $\Omega_\pm$ that coincides with Γ by $\Gamma_\pm$ (see Figure 1), such that for functions $\boldsymbol{z} : \Omega \to \mathbb{R}^m$ we can define one-sided limits $\boldsymbol{z}_\pm = \boldsymbol{z}|_{\Gamma_\pm}$. However, we

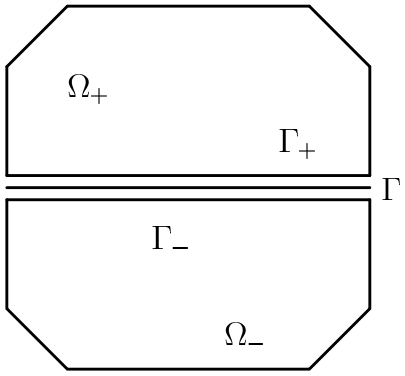

Figure 1: Body $\Omega = \Omega_+ \cup \Omega_-$ with interface Γ.

also allow for extra fields $\boldsymbol{z}_\Gamma : \Gamma \to \mathbb{R}^k$ describing new species or some of the species on Ω, i.e. we allow for $k \neq m$.

The full state is $Z = (\boldsymbol{z}, \boldsymbol{z}_\Gamma)$ containing bulk functions as well as interface functions. We derive our coupled system again in the Onsager form $\dot{Z} = -\mathcal{K}(Z)\mathrm{D}\Phi(Z)$, where now the driving functional Φ as well as the dual dissipation potential Ψ^*, which defines $\mathcal{K}$, are given in terms of a bulk integral and an interface integral:

$$\Phi(Z) = \Phi_\Omega(\boldsymbol{z}) + \Phi_\Gamma(\widehat{\boldsymbol{z}}) \text{ with } \widehat{\boldsymbol{z}} := (\boldsymbol{z}_\Gamma, \boldsymbol{z}_+, \boldsymbol{z}_-) \quad \text{and}$$
$$\Psi^*(\boldsymbol{z}, \boldsymbol{z}_\Gamma; \boldsymbol{\xi}, \boldsymbol{\xi}_\Gamma) = \Psi^*_\Omega(\boldsymbol{z}; \boldsymbol{\xi}) + \Psi^*_\Gamma(\widehat{\boldsymbol{z}}; \widehat{\boldsymbol{\xi}}) \text{ with } \widehat{\boldsymbol{\xi}} = (\boldsymbol{\xi}_\Gamma, \boldsymbol{\xi}_+, \boldsymbol{\xi}_-).$$

While the bulk integrals Φ_Ω and Ψ^*_Ω only depend on the bulk fields $\boldsymbol{z}$ and the bulk forces $\boldsymbol{\xi}$, respectively, the interface integrals Φ_Γ and Ψ^*_Γ depend on the interface fields $\boldsymbol{z}_\Gamma$ and $\boldsymbol{\xi}_\Gamma$ as well as on the one-sided interface limits $\boldsymbol{z}_\pm$ and $\boldsymbol{\xi}_\pm$.

The general Onsager system is now defined as

$$\begin{pmatrix} \dot{\boldsymbol{z}} \\ \dot{\boldsymbol{z}}_\Gamma \end{pmatrix} = \mathrm{D}_{(\boldsymbol{\xi}, \boldsymbol{\xi}_\Gamma)} \Psi^*\big(\boldsymbol{z}, \boldsymbol{z}_\Gamma\,,\, -\mathrm{D}_{\boldsymbol{z}, \boldsymbol{z}_\Gamma} \Phi(\boldsymbol{z}, \boldsymbol{z}_\Gamma)\big),$$

where the derivative $\mathrm{D}_{(\boldsymbol{\xi}, \boldsymbol{\xi}_\Gamma)}\Psi^*$ involves integrations by part which give rise to nontrivial coupling conditions on Γ. We will first display this in a scalar heat equation and then treat a more general case.

We refer to [Bed86, KjB08] for careful treatments of thermochemical effects at interfaces. The works also provide evidence for the physical necessity to introduce own species and temperature fields on the interface.

4.2 Coupled bulk and interface heat conduction

We assume that the only relevant variable is the temperature, but there is a temperature $\theta : \Omega \to]0, \infty[$ in the bulk and another independent temperature $\theta_\Gamma : \Gamma \to]0, \infty[$ in the interface. This may model for instance a thin steel plate Γ inside a rubber material. The total entropy and total energy are given via

$$\mathcal{S}(\theta, \theta_\Gamma) = \int_\Omega c \log \theta \,\mathrm{d}x + \int_\Gamma c_\Gamma \log \theta_\Gamma \,\mathrm{d}a \quad \text{and} \quad \mathcal{E}(\theta, \theta_\Gamma) = \int_\Omega c\,\theta \,\mathrm{d}x + \int_\Gamma c_\Gamma \theta_\Gamma \,\mathrm{d}a,$$

where $c > 0$ is the specific heat of the bulk material (per unit volume) and $c_\Gamma > 0$ is the specific heat of the interface material (per unit surface area). These specific heats may also depend on $x \in \Omega$ or $y \in \Gamma$.

For the dissipation potential we assume the simplest quadratic form

$$\Psi^*(\theta, \theta_\Gamma, \tau, \tau_\Gamma) = \int_\Omega \frac{k}{2} |\nabla(\frac{\tau}{c})|^2 \mathrm{d}x + \Psi^*_\Gamma(\widehat{\theta}, \widehat{\tau}) \quad \text{with}$$
$$\Psi^*_\Gamma(\widehat{\theta}, \widehat{\tau}) = \textstyle\int_\Gamma \frac{k_\Gamma}{2} |\nabla_\Gamma(\frac{\tau_\Gamma}{c_\Gamma})|^2 + \frac{m_\Gamma}{2}\big(\frac{\tau_+}{c_+} - \frac{\tau_-}{c_-}\big)^2 + \frac{m_+}{2}\big(\frac{\tau_+}{c_+} - \frac{\tau_\Gamma}{c_\Gamma}\big)^2 + \frac{m_-}{2}\big(\frac{\tau_-}{c_-} - \frac{\tau_\Gamma}{c_\Gamma}\big)^2 \mathrm{d}a,$$

where k may depend on $x \in \Omega$ and θ and k_Γ, m_Γ, and $m_\pm$ may depend on $y \in \Gamma$ and $\widehat{\theta} := (\theta_\Gamma, \theta_+, \theta_-)$. Here k_Γ denotes the heat conduction coefficient in the interface, m_Γ gives a condition for heat transmission through the interface, whereas $m_\pm$ gives heat flow from the bulk into the interface.

With $\Theta = (\theta, \theta_\Gamma)$ the Onsager system $\dot{\Theta} = \mathcal{K}(\Theta)\mathrm{D}\mathcal{S}(\Theta)$ takes the form

$$\begin{aligned}
&\text{in } \Omega: && \dot\theta \;= -\frac{1}{c}\operatorname{div}\big(k\nabla\frac{1}{\theta}\big),\\
&\text{in } \Gamma: && \dot\theta_\Gamma = -\tfrac{1}{c_\Gamma}\operatorname{div}_\Gamma\big(k_\Gamma\nabla_\Gamma\tfrac{1}{\theta_\Gamma}\big) + m_+\big(\tfrac{1}{\theta_\Gamma}-\tfrac{1}{\theta_+}\big) + m_-\big(\tfrac{1}{\theta_\Gamma}-\tfrac{1}{\theta_-}\big),\\
&\text{in } \Gamma_+: && 0 \;= \tfrac{1}{c_+}k_+\nabla\tfrac{1}{\theta}\cdot\nu_+ - m_+\big(\tfrac{1}{\theta_\Gamma}-\tfrac{1}{\theta_+}\big) - m_\Gamma\big(\tfrac{1}{\theta_-}-\tfrac{1}{\theta_+}\big),\\
&\text{in } \Gamma_-: && 0 \;= \tfrac{1}{c_-}k_-\nabla\tfrac{1}{\theta}\cdot\nu_- - m_-\big(\tfrac{1}{\theta_\Gamma}-\tfrac{1}{\theta_-}\big) - m_\Gamma\big(\tfrac{1}{\theta_+}-\tfrac{1}{\theta_-}\big).
\end{aligned}$$

Recall that we are dealing with closed systems, hence we also have the no-flux condition $k\nabla(1/\theta)\cdot\nu = 0$ on the outer boundary $\partial(\Omega\cup\Gamma)$. This coupled system contains the usual bulk equation which is coupled to the interface by Robin-type boundary conditions that depend on the temperatures inside the interface Γ and on the limit of the bulk temperature on the other side of the interface. Moreover, there is an own heat equation on the interface where the flux terms from the boundary appear as source terms.

The above general nonlinear system also includes a linear system if we choose

$$k(\theta) = \theta^2\kappa^\Omega, \quad k_\Gamma(\widehat{\theta}) = \theta_\Gamma^2\kappa^\Gamma, \quad m_\pm(\widehat{\theta}) = \mu_\pm\theta_\pm\theta_\Gamma, \quad m_\Gamma(\widehat{\theta}) = \mu_\Gamma\theta_+\theta_-.$$

We obtain the linear system

$$\begin{aligned}
&\text{in } \Omega: && c\dot\theta \;= \operatorname{div}\big(\kappa^\Omega\nabla\theta\big),\\
&\text{in } \Gamma: && c_\Gamma\dot\theta_\Gamma = \operatorname{div}_\Gamma\big(\kappa^\Gamma\nabla_\Gamma\theta_\Gamma\big) + c_\Gamma\mu_+(\theta_+-\theta_\Gamma) + c_\Gamma\mu_-(\theta_--\theta_\Gamma),\\
&\text{in } \Gamma_+: && 0 \;= \tfrac{1}{c_+}\kappa^\Omega_+\nabla\theta\cdot\nu_+ + \mu_+(\theta_+-\theta_\Gamma) + \mu_\Gamma(\theta_+-\theta_-),\\
&\text{in } \Gamma_-: && 0 \;= \tfrac{1}{c_-}\kappa^\Gamma_-\nabla\theta\cdot\nu_- + \mu_-(\theta_--\theta_\Gamma) + \mu_\Gamma(\theta_--\theta_+).
\end{aligned}$$

4.3 General structure of bulk-interface interaction

We now return to the general case of bulk-interface systems with the state $Z = (\boldsymbol{z}, \boldsymbol{z}_\Gamma)$ and a driving functional specified in the form

$$\mathcal{F}(Z) = \mathcal{F}_\Omega(\boldsymbol{z}) + \mathcal{F}_\Gamma(\widehat{\boldsymbol{z}}) = \int_\Omega F_\Omega(\boldsymbol{z}, \nabla\boldsymbol{z})\,\mathrm{d}x + \int_\Gamma F_\Gamma(\widehat{\boldsymbol{z}}, \nabla_\Gamma\boldsymbol{z}_\Gamma)\,\mathrm{d}a,$$

where as before $\widehat{\boldsymbol{z}} = (\boldsymbol{z}_\Gamma, \boldsymbol{z}_+, \boldsymbol{z}_-)$. To include Allen-Cahn and Cahn-Hilliard systems we allow $\mathcal{F}$ to depend on the gradients $\nabla\boldsymbol{z}$ and $\nabla_\Gamma\boldsymbol{z}_\Gamma$ as well.

For the dual dissipation potential we also specify the structure more explicitly, namely

$$\begin{aligned}
&\Psi^*(Z;\Xi) = \Psi^*_\Omega(\boldsymbol{z};\boldsymbol{\xi}) + \Psi^*_\Gamma(\widehat{\boldsymbol{z}};\widehat{\boldsymbol{\xi}}) \text{ with } \widehat{\boldsymbol{\xi}} = (\boldsymbol{\xi}_\Gamma, \boldsymbol{\xi}_+, \boldsymbol{\xi}_-),\\
&\Psi^*_\Omega(\boldsymbol{z};\boldsymbol{\xi}) = \int_\Omega \frac{1}{2}\nabla\boldsymbol{\xi}{:}\mathbb{M}(\boldsymbol{z}){:}\nabla\boldsymbol{\xi} + \frac{1}{2}\boldsymbol{\xi}{\cdot}\mathbb{H}(\boldsymbol{z})\boldsymbol{\xi}\,\mathrm{d}x, \text{ and}\\
&\Psi^*_\Gamma(\widehat{\boldsymbol{z}},\widehat{\boldsymbol{\xi}}) = \int_\Gamma \frac{1}{2}\nabla_\Gamma\boldsymbol{\xi}_\Gamma{:}\mathbb{M}_\Gamma(\widehat{\boldsymbol{z}}){:}\nabla_\Gamma\boldsymbol{\xi}_\Gamma + \frac{1}{2}\widehat{\boldsymbol{\xi}}{\cdot}\mathbb{T}(\widehat{\boldsymbol{z}})\widehat{\boldsymbol{\xi}}\,\mathrm{d}a.
\end{aligned}$$

To write the Onsager system $\dot{Z} = -\mathrm{D}_\Xi\Psi^*(Z;\mathrm{D}\mathcal{F}(Z))$ more explicity, we use the natural projections Q_Γ, Q_+, Q_- associated with the components of $\widehat{\boldsymbol{z}} = (\boldsymbol{z}_\Gamma, \boldsymbol{z}_+, \boldsymbol{z}_-)$. Using the variational derivatives

$$\delta_{\boldsymbol{z}}F_\Omega := \partial_{\boldsymbol{z}}F_\Omega - \operatorname{div}\big(\partial_{\nabla\boldsymbol{z}}F_\Omega\big) \quad\text{and}\quad \delta_{\boldsymbol{z}_\Gamma}F_\Gamma := \partial_{\boldsymbol{z}_\Gamma}F_\Gamma - \operatorname{div}_\Gamma\big(\partial_{\nabla_\Gamma\boldsymbol{z}_\Gamma}F_\Gamma\big)$$

and suitable integrations by part the general bulk-interface system in Onsager form reads

$$\begin{aligned}
\text{in } \Omega: \quad \dot{\boldsymbol{z}} &= -\operatorname{div}\Big(\mathbb{M}_\Omega(\boldsymbol{z})\nabla\big(\delta_{\boldsymbol{z}}F_\Omega\big)\Big) - \mathbb{H}(\boldsymbol{z})\big(\delta_{\boldsymbol{z}}F_\Omega\big),\\
\text{in } \Gamma: \quad \dot{\boldsymbol{z}}_\Gamma &= -\operatorname{div}_\Gamma\Big(\mathbb{M}_\Gamma(\widehat{\boldsymbol{z}})\nabla\big(\delta_{\boldsymbol{z}_\Gamma}F_\Gamma\big)\Big) - Q_\Gamma\mathbb{T}(\widehat{\boldsymbol{z}})\big(\delta_{\widehat{\boldsymbol{z}}}F_\Gamma, \delta_{\boldsymbol{z}}F_\Omega|_{\Gamma_+}, \delta_{\boldsymbol{z}}F_\Omega|_{\Gamma_-}\big),\\
\text{in } \Gamma_+: \quad 0 &= \mathbb{M}_\Omega(\boldsymbol{z})\nabla\big(\delta_{\boldsymbol{z}}F_\Omega\big)\cdot\nu_+ + Q_+\mathbb{T}(\widehat{\boldsymbol{z}})\big(\delta_{\widehat{\boldsymbol{z}}}F_\Gamma, \delta_{\boldsymbol{z}}F_\Omega|_{\Gamma_+}, \delta_{\boldsymbol{z}}F_\Omega|_{\Gamma_-}\big),\\
\text{in } \Gamma_+: \quad 0 &= \mathbb{M}_\Omega(\boldsymbol{z})\nabla\big(\delta_{\boldsymbol{z}}F_\Omega\big)\cdot\nu_- + Q_-\mathbb{T}(\widehat{\boldsymbol{z}})\big(\delta_{\widehat{\boldsymbol{z}}}F_\Gamma, \delta_{\boldsymbol{z}}F_\Omega|_{\Gamma_+}, \delta_{\boldsymbol{z}}F_\Omega|_{\Gamma_-}\big).
\end{aligned} \tag{4.1}$$

We refer to [GlM11, Thm. 3.1] for a proof of the equivalence of (4.1) and the Onsager system $\dot{Z} = -\mathrm{D}_\Xi\Psi^*(Z;\mathrm{D}\mathcal{F}(Z))$ with the potentials $\mathcal{F}$ and Ψ^* as defined above.

4.4 Semiconductors with interfaces for photovoltaics

In thin-film solar cells the interfaces strongly influence the overall currents of the whole solar cell. Hence a proper modeling of the interaction between the bulk and the interface effects is necessary. In addition to the previous analysis, we also need to take into account the electrical charges of the species, namely the free electrons with density n and the holes with density p.

In the simplest case the bulk model is the so-called van Roosbroeck system, which couples an equation for the electrostatic potential $\phi = \phi_{\boldsymbol{u}}$ with the drift-diffusion-reaction equations for $\boldsymbol{u} = (n, p)$:

$$\text{(vRS)} \quad \begin{cases} -\operatorname{div}(\varepsilon\nabla\phi_{\boldsymbol{u}}) = d_\Omega(x) - n + p,\\ \dot{n} = \operatorname{div}\Big(m_n\big(\nabla n - n\,\nabla\phi_{\boldsymbol{u}}\big)\Big) - k\,(np-1),\\ \dot{p} = \operatorname{div}\Big(m_p\big(\nabla p + p\,\nabla\phi_{\boldsymbol{u}}\big)\Big) - k\,(np-1). \end{cases} \tag{4.2}$$

The different signs in "$-n$" and "$+p$" in the Poisson equation for $\phi_{\boldsymbol{u}}$ and in front of the drift term $\nabla\phi_{\boldsymbol{u}}$ denote the negative charge of the electrons and the positive charge of the holes. Here ε is the electric permittivity, and d_Ω is a prescribed doping profile of charges. The coefficients m_p and m_n are the mobilities of the electrons and holes, respectively, and k is the reaction strength. Without loss of generality, we have normalized the densities

such that the intrinsic density equals $n_{\mathrm{in}} = 1$. On the boundary we add no-flux conditions for the charges and Dirichlet conditions for the electrostatic potential $\phi_{\boldsymbol{u}}$.

It is shown in [Mie11b, Sect. 4.1] that (4.2) forms an Onsager system for the total free energy $\mathcal{F}_\Omega$ and the dual dissipation potential Ψ^*_Ω given by

$$\mathcal{F}_\Omega(n,p) = \int_\Omega \frac{\varepsilon}{2}|\nabla\phi_{n,p}|^2 + \lambda(n) + \lambda(p)\,\mathrm{d}x, \tag{4.3a}$$

$$\Psi^*_\Omega(\boldsymbol{u},\boldsymbol{\mu}) = \frac{1}{2}\int_\Omega m_n\, n|\nabla\mu_n|^2 + m_p\, p|\nabla\mu_p|^2 + k\,\Lambda(np,1)(\mu_n+\mu_p)^2\,\mathrm{d}x, \tag{4.3b}$$

where Λ is defined in (3.4).

Following [GlM11] we now consider a domain Ω with one or several interfaces denoted by $\Gamma \subset \overline{\Omega}$. Thin-film solar cells have a thickness of a few hundred nanometers and contain several interfaces. These are treated in particular ways in order to make them active in the sense that they carry own interfacial species which may diffuse and react inside the interface or with species from the adjacent sides $\Gamma_\pm$ from the bulk. A particular reaction is the simple capture and escape of species from the interface into the bulk, which is then called thermionic emission.

For notational simplicity we assume here that the interface species are simply $\boldsymbol{u}_\Gamma = (n_\Gamma, p_\Gamma) : \Gamma \to]0,\infty[^2$ and hasten to say that $\boldsymbol{u}_\Gamma$ is in general different from the one-sided limits $\boldsymbol{u}_+ = \boldsymbol{u}|_{\Gamma_+}$. We will write $U = (\boldsymbol{u}, \boldsymbol{u}_\Gamma)$ for the full state of the bulk-interface system. Moreover, the interface may carry its own doping profile d_Γ such that the joint electrostatic potential $\phi = \phi_U$ satisfies the Poisson equation

$$-\operatorname{div}(\varepsilon\nabla\phi_U) = d_\Omega - n + p + (\delta_\Gamma - n_\Gamma + p_\Gamma)\delta_\Gamma,$$

where δ_Γ denotes the two-dimensional Hausdorff measure restricted to the interface Γ. Thus, the potential ϕ_U depends on the bulk and the interface charges in a linear way.

The total free energy now consists of the bulk part $\mathcal{F}_\Omega$ from (4.3a) and an interface part, namely

$$\mathcal{F}(\boldsymbol{u},\boldsymbol{u}_\Gamma) = \int_\Omega \frac{\varepsilon}{2}|\nabla\phi_{\boldsymbol{u},\boldsymbol{u}_\Gamma}|^2 + \lambda(n) + \lambda(p)\,\mathrm{d}x + \int_\Gamma \lambda(n_\Gamma) + \lambda(p_\Gamma)\,\mathrm{d}a.$$

The corresponding differential $\mathrm{D}\mathcal{F}$ takes the form

$$\begin{pmatrix}\boldsymbol{\mu}\\ \boldsymbol{\mu}_\Gamma\end{pmatrix} := \mathrm{D}\mathcal{F}(\boldsymbol{u},\boldsymbol{u}_\Gamma) = \begin{pmatrix}\mathrm{D}_{\boldsymbol{u}}\mathcal{F}(\boldsymbol{u},\boldsymbol{u}_\Gamma)\\ \mathrm{D}_{\boldsymbol{u}_\Gamma}\mathcal{F}(\boldsymbol{u},\boldsymbol{u}_\Gamma)\end{pmatrix} = \begin{pmatrix}\log\boldsymbol{u} + \binom{-1}{1}\phi_U\\ \log\boldsymbol{u}_\Gamma + \binom{-1}{1}\phi_U|_\Gamma\end{pmatrix}.$$

To define a sufficiently general dual dissipation potential Ψ^*, which contains the bulk part Ψ^*_Ω from (4.3b) as well as an interfacial terms, we use again the abbreviations $\widehat{\boldsymbol{u}} := (\boldsymbol{u}_\Gamma, \boldsymbol{u}_+, \boldsymbol{u}_-)$ and $\widehat{\boldsymbol{\mu}} := (\boldsymbol{\mu}_\Gamma, \boldsymbol{\mu}_+, \boldsymbol{\mu}_-)$ and set

$$\Psi^*(\boldsymbol{u},\boldsymbol{u}_\Gamma;\boldsymbol{\mu},\boldsymbol{\mu}_\Gamma) = \Psi^*_\Omega(\boldsymbol{u},\boldsymbol{\mu}) + \Psi^*_\Gamma(\widehat{\boldsymbol{u}};\widehat{\boldsymbol{\mu}}) \text{ with}$$

$$\Psi^*_\Gamma(\widehat{\boldsymbol{u}};\widehat{\boldsymbol{\mu}}) = \Psi^*_{\text{in-plane}}(\widehat{\boldsymbol{u}};\widehat{\boldsymbol{\mu}}) + \Psi^*_{\text{transfer}}(\widehat{\boldsymbol{u}};\widehat{\boldsymbol{\mu}}),$$

$$\Psi^*_{\text{in-plane}}(\widehat{\boldsymbol{u}};\widehat{\boldsymbol{\mu}}) = \frac{1}{2}\int_\Gamma m_n^\Gamma n_\Gamma|\nabla_\Gamma\mu_{\Gamma\,n}|^2 + m_p^\Gamma p_\Gamma|\nabla_\Gamma\mu_{\Gamma\,p}|^2 + \boldsymbol{\mu}_\Gamma\cdot\mathbb{H}^\Gamma(\widehat{\boldsymbol{u}})\cdot\boldsymbol{\mu}_\Gamma\,\mathrm{d}a,$$

$$\Psi^*_{\text{transfer}}(\widehat{\boldsymbol{u}};\widehat{\boldsymbol{\mu}}) = \frac{1}{2}\int_\Gamma T(\widehat{\boldsymbol{u}})|\boldsymbol{\mu}_+-\boldsymbol{\mu}_-|^2 + B_+(\widehat{\boldsymbol{u}})|\boldsymbol{\mu}_+-\boldsymbol{\mu}_\Gamma|^2 + B_-(\widehat{\boldsymbol{u}})|\boldsymbol{\mu}_--\boldsymbol{\mu}_\Gamma|^2\,\mathrm{d}a.$$

Here $\Psi^*_{\text{in-plane}}$ contains all dissipative effects that solely occur inside of Γ, while Ψ^*_{transfer} provides the coefficients for movements between Γ, Γ_+, and Γ_-. In particular, T is the intensity of the transmissions between Γ_+ and Γ_-, and $B_\pm$ is the intensity for motions between $\Gamma_\pm$ and Γ.

As was indicated in Section 4.3 the coupled system has the form

$$
\begin{aligned}
\text{in } \Omega: \quad & 0 = -\operatorname{div}(\varepsilon\nabla\phi_{\boldsymbol{u},\boldsymbol{u}_\Gamma}) - (d_\Omega - n + p) - (d_\Gamma - n_\Gamma + p_\Gamma)\delta_\Gamma,\\
\text{in } \Omega: \quad & \dot{\boldsymbol{u}} = \operatorname{div}\big(M(\boldsymbol{u})\nabla\boldsymbol{\mu}\big) - \mathbb{H}(\boldsymbol{u})\boldsymbol{\mu} \quad (= \text{van Roosbroeck system})\\
\text{in } \Gamma_+: \quad & 0 = M_+\nabla\boldsymbol{\mu}_+\cdot\nu_+ - T(\widehat{\boldsymbol{u}})(\boldsymbol{\mu}_+ - \boldsymbol{\mu}_-) - B_+(\widehat{\boldsymbol{u}})(\boldsymbol{\mu}_+ - \boldsymbol{\mu}_\Gamma),\\
\text{in } \Gamma: \quad & \dot{\boldsymbol{u}}_\Gamma = \underbrace{\operatorname{div}_\Gamma\big(M_\Gamma\nabla_\Gamma\boldsymbol{\mu}_\Gamma\big)}_{\text{interfacial drift-diffusion}} - \underbrace{\mathbb{H}^\Gamma(\widehat{\boldsymbol{u}})\boldsymbol{\mu}_\Gamma}_{\text{interfacial reaction}} - \underbrace{B_+(\boldsymbol{\mu}_\Gamma - \boldsymbol{\mu}_+) - B_-(\boldsymbol{\mu}_\Gamma - \boldsymbol{\mu}_-)}_{\text{transfer between } \Gamma \text{ and } \Gamma_+\cup\Gamma_-}\\
\text{in } \Gamma_-: \quad & 0 = M_-\nabla\boldsymbol{\mu}_-\cdot\nu_- - T(\widehat{\boldsymbol{u}})(\boldsymbol{\mu}_- - \boldsymbol{\mu}_+) - B_-(\widehat{\boldsymbol{u}})(\boldsymbol{\mu}_- - \boldsymbol{\mu}_\Gamma).
\end{aligned}
$$

We conclude by summarizing this section. The structure of Onsager system is sufficiently rich to derive energy-reaction-diffusion system including possible bulk-interface interactions. Using the abstract form of Onsager systems specified in terms of bulk and interface integrals it is straight forward to derive thermomechanically consistent coupled systems. The derived equations are in general nonlinear coupled systems, the analysis of which still needs to be developed.

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