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A gradient structure for reaction-diffusion systems and for energy-drift-diffusion systems

Dedicated to Herbert Gajewski on the occasion of his 70th birthday

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Abstract

In recent years the theory of the Wasserstein metric has opened up a new treatments of the diffusion equations as gradient systems, where the free energy or the entropy take the role of the driving functional and where the space is equipped with the Wasserstein metric. We show on the formal level that this gradient structure can be generalized to reaction-diffusion systems with reversible mass-action kinetic. The metric is constructed by using the dual dissipation potential, which is a quadratic functional of all chemical potentials including the mobilities as well as the reaction kinetics. The metric structure is obtained by Legendre transform from the dual dissipation potential.

The same ideas extend to systems including electrostatic interactions or a correct energy balance via coupling to the heat equation. We show this by treating the semiconductor equations involving the electron and hole densities, the electrostatic potential, and the temperature. Thus, the models in [AGH02], which stimulated this work, have a gradient structure.

1 Introduction

In the seminal work of Otto [Ott98, JKO98, Ott01] it was shown that certain diffusion equations can be interpreted as gradient flows with respect to the physically relevant free energy or the entropy as a driving functional. The difficulty is that the associated Riemannian metric is rather weak, namely a weighted H^{-1} norm, where the weight depends on the state itself. In the scalar case it turned out that the associated distance is well-defined and can be characterized as the Wasserstein distance, which is well-established in transportation theory, see [AGS05] for a survey. However, to the author's best knowledge there is no corresponding theory of gradient structures for systems of reaction-diffusion equations. For coupled diffusion systems joint gradient structures seems to be common knowledge, although they are rarely highlighted.

The major obstructions to the construction of gradient structures for reaction-diffusion systems arise from the reaction terms, since the reaction kinetics can lead to quite general nonlinearities. It is well know that for large classes for reaction systems there exists (convex) Liapunov functions, namely the free energy of the negative entropy, and thus it can be shown that all solutions converge to equilibria. Here we want to complete the theory by showing that for certain classes we can even give a gradient structure. The motivation for the present work are the thermodynamical models for semiconductors derived in [AGH02]. In this work the reaction terms were written in a very special form involving the associated chemical potentials. The observation of the present work is that these reaction terms can be written the derivative of a (dual dissipation) potential ψ^* with respect to the chemical potentials, see Remark 4.1. For consistency and wider application we will use a slightly different form in this work.

In this work we establish a gradient structure for certain reaction-diffusion systems as well as for systems coupled with the heat equation. However, we simply establish the formal Riemannian structure, more precisely its inverse, which we call the ***dual dissipation potential***. From there it is possible to characterize the corresponding weak Riemannian structure by solving the associated elliptic problem with state-dependent coefficients. The subsequent characterization of the associated distance between different states would be desirable for the case of reaction-diffusion systems as well, however, this goes far beyond the present work.

All material in this short paper will be purely formal and will not address the question in which function spaces the objects are well defined or in which spaces the problem is well-posed. We simply concentrate on the formal manipulations and choices which have to be done to obtain functionals given a formal gradient structure. It is expected that these formulations will have future impact on the analysis of such systems, for instance on the construction of solutions via the metric approach (see [AGS05]) or on the construction of suitable space-time discretizations preserving not only positivity and energy decay (as in [Gli09, GlG09]) but also the full gradient structure.

To explain the main ideas of the paper we start with the general notion of gradient systems. A triple $(\boldsymbol{Z}, \Phi, \Psi)$ is called a gradient system if the state space $\boldsymbol{Z}$ is a Hilbert space, $\Phi : \boldsymbol{Z} \to \mathbb{R}_\infty := \mathbb{R} \cup \{\infty\}$ is the driving functional, and Ψ is the dissipation potential with the quadratic form $\Psi(\boldsymbol{z}, \dot{\boldsymbol{z}}) = \frac{1}{2}\langle \boldsymbol{G}(\boldsymbol{z})\dot{\boldsymbol{z}}, \dot{\boldsymbol{z}}\rangle$. The evolution is given in the form

$$\boldsymbol{G}(z)\dot{\boldsymbol{z}} = -\mathrm{D}\Phi(\boldsymbol{z}) \quad \text{or equivalently} \quad \dot{\boldsymbol{z}} = -\nabla^{\boldsymbol{G}}\Phi(\boldsymbol{z}) := -\boldsymbol{G}(\boldsymbol{z})^{-1}\mathrm{D}\Phi(\boldsymbol{z}). \tag{1.1}$$

Note that this equation can be seen as a force balance between friction forces and potential restoring forces. For our work it is crucial to work this the dual form obtained via the dual dissipation potential $\Psi^*(\boldsymbol{z}, \cdot) : \boldsymbol{Z}^* \to [0, \infty]$ obtained from $\Psi(\boldsymbol{z}, \cdot) : \boldsymbol{Z} \to [0, \infty]$ via Legendre transform:

$$\Psi^*(\boldsymbol{z}, \boldsymbol{\mu}) = \frac{1}{2}\langle \boldsymbol{\mu}, \boldsymbol{G}(\boldsymbol{z})^{-1}\boldsymbol{\mu}\rangle.$$

The ***dual gradient structure*** is then given as the rate equation

$$\dot{\boldsymbol{z}} = \mathrm{D}\Psi^*(\boldsymbol{z}, -\mathrm{D}\Phi(\boldsymbol{z})) = -\boldsymbol{G}(\boldsymbol{z})^{-1}\mathrm{D}\Phi(\boldsymbol{z}). \tag{1.2}$$

The point of our work is to establish suitable functionals Φ and dual dissipation potentials Ψ^* such that reaction diffusion systems of the type

$$\dot{\boldsymbol{n}} = \operatorname{div}\big(M(\boldsymbol{n})\nabla\boldsymbol{n}\big) + \boldsymbol{R}(\boldsymbol{n}) \tag{1.3}$$

can be written as a dual gradient system in the sense of (1.2).

In fact, there is a rich literature (see e.g. [Grö83, GGH96, GlH97, DeF06, DeF07, Gli08, BDS09]) on energy-entropy estimates for reaction-diffusion systems, which establish decay of solutions to the unique steady state under given constraints. In these works the driving functionals are just used as Liapunov function; and its interplay with the dissipation potential gives convergence. Here we show that in many of the considered cases there is even an exact gradient structure. Thus, there is future potential to apply the more advanced variational theory for gradient systems. On the long run, the results of present work have the potential to improve on sharpen these results, since it becomes evident that the functionals used as Liapunov functionals only, are in fact driving functionals in a gradient system.

Our motivation and the the fundamental ideas to treat a sufficiently large class of reaction-diffusion equations came from the work [AGH02], where energy-electro-reaction-diffusion systems for semiconductors where treated. The reactions (also called recombinations in the semiconductor context) are strongly reversible reactions according to mass-action kinetics, cf. [FeH77, Grö83, ErT89]. This means that the reaction coefficient for the forward and the backward reaction are the same. This microscopic reversibility is a good assumption for elementary reactions on the microscopic and nanoscopic level, but there are many macroscopic models that do not fall into this class.

As an example consider a model with two species X_1 and X_2 and the reaction

$$\alpha_1 X_1 + \alpha_2 X_2 \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \beta_1 X_1 + \beta_2 X_2.$$

The associated reaction-diffusion systems for the densities $\boldsymbol{n} = (n_1, n_2)$ reads

$$\begin{aligned} \dot{n}_1 &= d_1 \Delta n_1 - (\alpha_1{-}\beta_1)\big(k_+ n_1^{\alpha_1} n_2^{\alpha_2} {-} k_- n_1^{\beta_1} n_2^{\beta_2}\big), \\ \dot{n}_2 &= d_2 \Delta n_2 - (\alpha_2{-}\beta_2)\big(k_+ n_1^{\alpha_1} n_2^{\alpha_2} {-} k_- n_1^{\beta_1} n_2^{\beta_2}\big). \end{aligned} \tag{1.4}$$

Our gradient structure uses the total free energy as the driving functional, namely

$$\mathcal{F}(\boldsymbol{n}) = \int_\Omega n_1(\log n_1{-}1) + n_2(\log n_2{-}1)\,\mathrm{d}x,$$

while the dual dissipation potential is the sum of Wasserstein-type mobility terms plus a reaction term, namely

$$\Psi^*(\boldsymbol{n}; \mu_1, \mu_2) = \frac{1}{2}\int_\Omega n_1 d_1 |\nabla\mu_1|^2 {+} n_2 d_2 |\nabla\mu_2|^2 {+} k_+ \ell(n_1^{\alpha_1} n_2^{\alpha_2}, n_1^{\beta_1} n_2^{\beta_2})\Big(\tbinom{\alpha_1-\beta_1}{\alpha_2-\beta_2}\cdot\tbinom{\mu_1}{\mu_2}\Big)^2\,\mathrm{d}x$$

with ℓ defined in (3.1). Using the ***strong reversibility conditions*** $k_+ = k_-$ it is easy to check that the dual gradient system $\dot{\boldsymbol{n}} = \mathrm{D}_{\boldsymbol{\mu}}\Psi^*(\boldsymbol{n}; -\mathrm{D}\mathcal{F}(\boldsymbol{n}))$ gives exactly (1.4).

In Section 3 we give generalizations of the above approach to arbitrary numbers of species and reactions, to systems with cross-diffusion, and to systems with weakly reversible reactions fulfilling the ***detailed balance condition***. In Section 3.5 we then consider reaction-diffusion systems coupled to a corresponding heat equation giving the exact energy balance. The driving functional is then the total entropy $\mathcal{S}$ while the total internal energy $\mathcal{E}$ provides a conserved quantity. It turns out that using the internal energy u as the thermodynamic state variable is much simpler than the more desirable temperature. However, it is one of the advantages of gradient systems, that transformation between different coordinate systems can be done with a reasonable amount of work.

Section 4 is devoted to electro-reaction-diffusion systems, where the species may be charged. The distribution of the charges generates an electrostatic potentials, whose electric field leads to additional drift contributions of the species proportional to their charge. In Section 4.1 we treat the simple isothermal van Roosbroeck system for the densities of electrons and holes only. In the final section is devoted to the full temperature-dependent semiconductor models devised in [AGH02]. We show that these models have a (dual) gradient structure. These models allow for an arbitrary number of charged species and arbitrary reversible reactions. Moreover, one can replace the Boltzmann statistics, which leads to the terms $n_i(\log n_i - 1)$, by the physically more appropriate Fermi-Dirac statistics.

2 Gradient formulations

We present different levels of the modeling in the form of generalized gradient flows. For a linear state space $\boldsymbol{Z}$ we consider a dissipation potential $\Psi(\boldsymbol{z}, \dot{\boldsymbol{z}})$, i.e., $\Psi : \mathrm{T}\boldsymbol{Z} \to [0, \infty]$. For each $\boldsymbol{z}$ the potential $\Psi(\boldsymbol{z}, \cdot) : \boldsymbol{Z} \to [0, \infty]$ satisfies $\Psi(\boldsymbol{z}, 0) = 0$ and is assumed to be lower semicontinuous and convex. Given an energy functional $\Phi : \boldsymbol{Z} \to \mathbb{R}$ the generalized gradient flow is given in the form

$$0 \in \partial_{\dot{\boldsymbol{z}}} \Psi(\boldsymbol{z}, \dot{\boldsymbol{z}}) + \mathrm{D}\Phi(\boldsymbol{z}) \quad \text{ in } \mathrm{T}^*_{\boldsymbol{z}}\boldsymbol{Z} \sim \boldsymbol{Z}^*. \tag{2.1}$$

In classical gradient flows, the dissipation potential has the quadratic form $\Psi(\boldsymbol{z}, \boldsymbol{v}) = \frac{1}{2}\langle \boldsymbol{G}(\boldsymbol{z})\boldsymbol{v}, \boldsymbol{v}\rangle$, where $\boldsymbol{G}(\boldsymbol{z}) : \mathrm{T}_{\boldsymbol{z}}\boldsymbol{Z} \to \mathrm{T}^*_{\boldsymbol{z}}\boldsymbol{Z}$ is a self-adjoint, positive definite operator. We then have the classical gradient-flow equation

$$\boldsymbol{G}(\boldsymbol{z})\dot{\boldsymbol{z}} = -\mathrm{D}\Phi(\boldsymbol{z}). \tag{2.2}$$

An equivalent formulation is obtained by using the Legendre transform $\Psi^*(\boldsymbol{z}, \cdot) = \mathcal{L}[\Psi(\boldsymbol{z}, \cdot)]$, namely $\Psi^*(\boldsymbol{z}, \boldsymbol{\zeta}) = \sup\{\, \langle \boldsymbol{\zeta}, \boldsymbol{v}\rangle - \Psi(\boldsymbol{z}, \boldsymbol{v}) \mid \boldsymbol{v} \in \boldsymbol{Z}\,\}$. Then, (2.1) is equivalent to the rate equation

$$\dot{\boldsymbol{z}} = \partial_{\boldsymbol{\zeta}} \Psi^*(\boldsymbol{z}, -\mathrm{D}\Phi(\boldsymbol{z})), \tag{2.3}$$

which in the classical gradient-flow case reads $\dot{\boldsymbol{z}} = -\boldsymbol{G}(\boldsymbol{z})^{-1}\mathrm{D}\Phi(\boldsymbol{z})$. The energy balance can be written in different ways

$$\begin{aligned}
\Phi(\boldsymbol{z}(0) - \Phi(\boldsymbol{z}(t)) &= \int_0^t \langle \partial_{\dot{\boldsymbol{z}}} \Psi(\boldsymbol{z}, \dot{\boldsymbol{z}}), \dot{\boldsymbol{z}}\rangle \,\mathrm{d}t &(2.4a)\\
&= \int_0^t \Psi(\boldsymbol{z}, \dot{\boldsymbol{z}}) + \Psi^*(\boldsymbol{z}, -\mathrm{D}\Phi(\boldsymbol{z}))\,\mathrm{d}t &(2.4b)\\
&= \int_0^t \langle -\mathrm{D}\Phi(\boldsymbol{z}), \partial_{\boldsymbol{\zeta}}\Psi^*(\boldsymbol{z}, -\mathrm{D}\Phi(\boldsymbol{z}))\rangle \,\mathrm{d}t. &(2.4c)
\end{aligned}$$

by using the classical Legendre equivalence

$$\boldsymbol{\zeta} \in \partial\mathcal{J}(\boldsymbol{v}) \iff \boldsymbol{v} \in \partial\mathcal{J}^*(\boldsymbol{\zeta}) \iff \mathcal{J}(\boldsymbol{z}) + \mathcal{J}^*(\boldsymbol{\zeta}) = \langle \boldsymbol{\zeta}, \boldsymbol{v}\rangle.$$

Since the right-hand sides in (2.4) represent the dissipated energy, we call Ψ the dissipation potential and Ψ^* the dual dissipation potential. Here (2.4b) plays a special role in the development of generalized gradient flows as it specifies the dynamics already completely.

Remark 2.1 (Transformation rule) *Often it is desirable to transform a gradient system for $\boldsymbol{z}$ via a transformation $\boldsymbol{z} = \phi(\boldsymbol{p})$, where $\phi : \boldsymbol{P} \to \boldsymbol{Z}$ is a local isomorphism. Given $(\boldsymbol{Z}, \Phi, \Psi)$ we define the gradient system $(\boldsymbol{P}, \widetilde{\Phi}, \widetilde{\Psi})$ via*

$$\widetilde{\Phi}(\boldsymbol{p}) = \Phi(\phi(\boldsymbol{p})) \quad \textit{and} \quad \widetilde{\Psi}(\boldsymbol{p}, \dot{\boldsymbol{p}}) = \Psi(\phi(\boldsymbol{p}), \mathrm{D}\phi(\boldsymbol{p})\dot{\boldsymbol{p}}).$$

Obviously, the two gradient systems are equivalent. Moreover we have

$$\widetilde{\boldsymbol{G}}(\boldsymbol{p}) = \mathrm{D}\phi(\boldsymbol{p})^* \boldsymbol{G}(\phi(\boldsymbol{p}))\mathrm{D}\phi(\boldsymbol{p}) \ \ \textit{and} \ \ \widetilde{\Psi}^*(\boldsymbol{p}, \boldsymbol{\mu}) = \Psi^*(\phi(\boldsymbol{p}), \mathrm{D}\phi(\boldsymbol{p})^{-*}\boldsymbol{\mu}).$$

In our applications for reaction-diffusion systems we will have two different types of gradient systems (i) isothermal systems with the (free) energy as driving functional and (ii) non-isothermal models with the entropy as driving functional.

In case (i) we usually write the gradient system $(\boldsymbol{Z}, \mathcal{F}, \Psi)$ in the dual form $\boldsymbol{n} = \mathrm{D}_{\boldsymbol{\mu}}\Psi^*(\boldsymbol{n}; -\mathcal{F}(\boldsymbol{n}))$, where $\boldsymbol{n}$ is the vector of densities of the species and $\boldsymbol{\mu} = \mathrm{D}\mathcal{F}(\boldsymbol{n})$ denotes the corresponding thermodynamic force dual to $\boldsymbol{n}$. The functional $\mathcal{F}$ is decreasing and $\Psi(\boldsymbol{n}; \dot{\boldsymbol{n}}) = \Psi^*(\boldsymbol{n}; -\mathrm{D}\mathcal{F}(\boldsymbol{n}))$ gives the energy-dissipation.

In case (ii) we use the entropy functional $\mathcal{S}$ as a function of the densities $\boldsymbol{n}$ and the internal energy u and have an additional conserved functional $\mathcal{E}(\boldsymbol{n}, u)$ is is the total energy. The thermodynamic forces are denoted by $\boldsymbol{\eta} = \mathrm{D}_{\boldsymbol{n}}\mathcal{S}(\boldsymbol{n}, u)$ and $\tau = \mathrm{D}_u\mathcal{S}(\boldsymbol{n}, u)$ such that, using standard thermodynamic conventions (cf. [AGH02, Mie10]) we find the absolute temperature $\theta = 1/\tau$ and the chemical potentials $\boldsymbol{\mu} = \theta\boldsymbol{\eta}$. The systems takes the form

$$(\dot{\boldsymbol{n}}, \dot{u}) = \mathrm{D}_{\boldsymbol{\eta},\tau}\Psi(\boldsymbol{n}, u; +\mathrm{D}\mathcal{S}(\boldsymbol{n}, u)), \tag{2.5}$$

where the "+" is because $-\mathcal{S}$ is a Liapunov function. The quantity $\Psi(\boldsymbol{n}, u; \dot{\boldsymbol{n}}, \dot{u}) = \Psi^*(\boldsymbol{n}, u; \mathrm{D}\mathcal{S}(\boldsymbol{n}, u))$ is called the entropy production.

Moreover, $\mathcal{E}$ is conserved along all solutions, if the invariance condition

$$\Psi^*(\boldsymbol{n}, u; (\boldsymbol{\eta}, \tau) + \lambda\mathrm{D}\mathcal{E}(\boldsymbol{n}, u)) = \Psi^*(\boldsymbol{n}, u; (\boldsymbol{\eta}, \tau)) \text{ for all } (\boldsymbol{n}, u), \ \lambda \in \mathbb{R} \tag{2.6}$$

holds. This relation obviously implies $\langle \mathrm{D}\mathcal{E}(\boldsymbol{n}, u), \mathrm{D}\Psi^*(\boldsymbol{n}, u; \boldsymbol{\eta}, \tau)\rangle = 0$, which leads to

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{E}(\boldsymbol{n}, u) = \langle \mathrm{D}\mathcal{E}(\boldsymbol{n}, u), (\dot{\boldsymbol{n}}, \dot{u})\rangle = \langle \mathrm{D}\mathcal{E}(\boldsymbol{n}, u), \mathrm{D}\Psi^*(\boldsymbol{n}, u; \mathrm{D}\mathcal{S}(\boldsymbol{\eta}, \tau)\rangle = 0. \tag{2.7}$$

In reaction-diffusion systems we will also have other conserved quantities such as atom or charge conservation.

In the case of a conserved energy $\mathcal{E}$ and possible further conserved functionals $\mathcal{C}_1, \ldots, \mathcal{C}_m$, one can use the ***principle of maximal entropy***, which means to maximize the (concave) entropy $\mathcal{S}$ under the constraints $\mathcal{E}(\boldsymbol{z}) = E_0$ and $\mathcal{C}_j(\boldsymbol{z}) = C_j$. Under suitable assumptions one obtains an extremum $\boldsymbol{z}_{\mathrm{eq}}$ and Lagrange multipliers $\lambda_0, \ldots, \lambda_m \in \mathbb{R}$ such that

$$0 = \mathrm{D}\mathcal{S}(\boldsymbol{z}_{\mathrm{eq}}) + \lambda_0\mathrm{D}\mathcal{E}(\boldsymbol{z}_{\mathrm{eq}}) + \lambda_1\mathrm{D}\mathcal{C}_1(\boldsymbol{z}_{\mathrm{eq}}) + \cdots + \lambda_m\mathrm{D}\mathcal{C}_m(\boldsymbol{z}_{\mathrm{eq}}).$$

Having an invariance (2.6) but now also including $\mathcal{C}_j$ it is easy to see that $\boldsymbol{z}_{\mathrm{eq}}$ is actually a steady state of the the gradient system (2.5).

3 Reaction-diffusion systems

The aim of this section is to show that reactions-diffusion systems of the type (1.2) may have a gradient structure, if the the reaction terms are generated from reversible reactions. The point is that the gradient structure is obtained in an indirect way using the dual gradient structure. It seems that this gradient structure is even unknown for the systems of ODEs describing the reactions without any diffusion.

3.1 Reversible reactions

We consider $\boldsymbol{n} = (n_1, \ldots, n_I) \in \mathbb{R}^I$ to be the densities of m different chemical species $X_1, \ldots, X_M$ reacting according to the mass action law, i.e. the reactions

$$\alpha_1^r X_1 + \cdots + \alpha_I^r X_I \underset{k_-^r}{\overset{k_+^r}{\rightleftharpoons}} \beta_1^r X_1 + \cdots + \beta_I^r X_I,$$

where $r = 1, ..., R$ is the number of possible reactions, $\boldsymbol{\alpha}^r, \boldsymbol{\beta}^r \in \mathbb{N}_0^I$ are the vectors of the stoichiometric coefficients, and k_+^r and k_-^r the positive forward and backward reaction rates, which may depend on $\boldsymbol{n}$ as well. The corresponding reaction kinetics is given by the ODE system

$$\dot{\boldsymbol{n}} = \boldsymbol{R}(\boldsymbol{n}) := \sum_{r=1}^{R} -\big(k_+^r(\boldsymbol{n})\boldsymbol{n}^{\boldsymbol{\alpha}^r} - k_-^r(\boldsymbol{n})\boldsymbol{n}^{\boldsymbol{\beta}^r}\big)\Big(\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r\Big),$$

where $\boldsymbol{n}^{\boldsymbol{\alpha}} = n_1^{\alpha_1} \cdots n_I^{\alpha_I}$, see [FeH77, Grö83, ErT89].

The rth reaction is called ***strongly reversible***, if $k_+^r = k_-^r$. If all reactions are reversible, i.e. $k_\pm^r = k^r$, then we can write the whole system as a gradient systems as follows. We define the free energy as $F(\boldsymbol{n}) = \sum_{i=1}^I n_i(\log n_i - 1)$, which gives the chemical potentials $\mathrm{D}F(\boldsymbol{n}) = \boldsymbol{\mu} = (\mu_1, \ldots, \mu_m) \in \mathbb{R}^I$ with $\mu_i = \log n_i$. We define the dual dissipation potential

$$\begin{aligned} \psi^*(\boldsymbol{n}, \boldsymbol{\mu}) &= \sum_{r=1}^{R} \frac{k^r(\boldsymbol{n})}{2} \ell(\boldsymbol{n}^{\boldsymbol{\alpha}^r}, \boldsymbol{n}^{\boldsymbol{\beta}^r}) \Big((\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r) \cdot \boldsymbol{\mu}\Big)^2 \\ \text{with } \ell(x, y) &= \begin{cases} \frac{x-y}{\log x - \log y} & \text{for } x \neq y, \\ y & \text{for } x = y. \end{cases} \end{aligned} \tag{3.1}$$

We note that the function $\ell :]0, \infty[^2 \to]0, \infty[$ is analytic. To check the identity $\boldsymbol{R}(\boldsymbol{n}) \equiv \mathrm{D}_{\boldsymbol{\mu}}\psi^*(\boldsymbol{n}, -\mathrm{D}F(\boldsymbol{n}))$ we simply exploit $\boldsymbol{\mu} \cdot \boldsymbol{\alpha} = \log(\boldsymbol{n}^{\boldsymbol{\alpha}})$.

The stoichiometric subspace $\mathbb{S}$ and its orthogonal complement $\mathbb{S}^\perp$ are defined via

$$\mathbb{S} := \mathrm{span}\{\, \boldsymbol{\alpha}^r - \boldsymbol{\beta}^r \mid r = 1, \ldots, R\,\} \subset \mathbb{R}^I, \quad \mathbb{S}^\perp := \{\, \boldsymbol{\xi} \in \mathbb{R}^I \mid \boldsymbol{\xi} \cdot \boldsymbol{\mu} = 0 \text{ for all } \boldsymbol{\mu} \in \mathbb{S}\,\}. \tag{3.2}$$

Then for each $\boldsymbol{\xi} \in \mathbb{S}^\perp$ the function $C_{\boldsymbol{\xi}}(\boldsymbol{n}) = \boldsymbol{\xi} \cdot \boldsymbol{n}$ defines a first integral, which is easily checked by using $\psi^*(\boldsymbol{n}, \boldsymbol{\mu} + \boldsymbol{\xi}) = \psi^*(\boldsymbol{n}, \boldsymbol{\mu})$. These conservation laws often go under the name ***conservation of atomic species***, see [ErT89].

Clearly, ψ^* can be written as the quadratic form

$$\psi^*(\boldsymbol{n}, \boldsymbol{\mu}) = \frac{1}{2}\boldsymbol{\mu} \cdot \boldsymbol{H}(\boldsymbol{n})\boldsymbol{\mu} \quad \text{with } \boldsymbol{H}(\boldsymbol{n}) \in \mathbb{R}^{I \times I}_{\text{spsd}},$$

where the subscript "spsd" denotes symmetric and positive semi-definite matrices. By the definition of the stoichiometric subspace and the positivity of k^r the mapping $\boldsymbol{H}(\boldsymbol{n})$ is strictly positive definite on $\mathbb{S}$. Thus, the Legendre transform $\psi(\boldsymbol{n}, \cdot) : \mathbb{R}^I \to [0, \infty]$ of $\psi^*(\boldsymbol{n}, \cdot) : \mathbb{R}^I \to [0, \infty[$ can be easily calculated in the form

$$\psi(\boldsymbol{n}, \boldsymbol{v}) = \begin{cases} \big(\frac{1}{2}\boldsymbol{H}(\boldsymbol{n})^+\boldsymbol{v}\big) \cdot \boldsymbol{v} & \text{for } \boldsymbol{v} \in \mathbb{S}, \\ \infty & \text{for } \boldsymbol{v} \notin \mathbb{S}, \end{cases} \tag{3.3}$$

where $\boldsymbol{H}^+$ denotes the pseudo inverse (Moore-Penrose inverse) of $\boldsymbol{H}$. Thus, the gradient systems reads

$$0 = \mathrm{D}_{\dot{\boldsymbol{n}}}\psi(\boldsymbol{n}, \dot{\boldsymbol{n}}) + \mathrm{D}F(\boldsymbol{n}).$$

The definition of ψ guarantees $\dot{\boldsymbol{n}} \in \mathbb{S}$ and thus the quantities C_ξ are conserved.

Remark 3.1 (Detailed balance) *The above gradient structure can be generalized to weakly reversible reactions, if the reactions have constant rates k_+^r and k_-^r which are **microscopically reversible**, or what is equivalent, they satisfy the **detailed balance condition**, i.e. there exists a steady state $\boldsymbol{n}_\circ = (n_1^\circ, \ldots, n_I^\circ) \in]0, \infty[^I$ such that*

$$k_\circ^r := k_+^r \boldsymbol{n}_\circ^{\boldsymbol{\alpha}^r} = k_-^r \boldsymbol{n}_\circ^{\boldsymbol{\beta}^r} \text{ for } r = 1, \ldots, R,$$

see [ErT89, p. 45]. Then, defining the relative free energy $F_\circ(\boldsymbol{n}) = \sum_{i=1}^I n_i(\log(n_i/n_i^\circ)-1)$ and $\psi_\circ^*(\boldsymbol{n}, \boldsymbol{\mu}) = \sum_{r=1}^R \frac{k_\circ^r}{2}\ell(\boldsymbol{n}^{\boldsymbol{\alpha}^r}/\boldsymbol{n}_\circ^{\boldsymbol{\alpha}^r}, \boldsymbol{n}^{\boldsymbol{\beta}^r}/\boldsymbol{n}_\circ^{\boldsymbol{\beta}^r})\big(\boldsymbol{\mu}\cdot(\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r)\big)^2$ gives the desired gradient structure.

Remark 3.2 (Relative entropy) *The above construction of $F_\circ$ can be understood in the sense of the "relative entropy". In many cases the (entropic part of the isothermal) free energy F can be written in the form $F(\boldsymbol{n}) = \sum_{i=1}^I \phi_i(n_i)$. For a given state $\boldsymbol{n}_\circ = (n_1^\circ, \ldots, n_I^\circ)$ the construction is $F_\circ(\boldsymbol{n}) = \sum_{i=1}^I \phi_i(n_i/n_i^\circ)n_i^\circ$.*

3.2 Diffusion system

For a given bounded and sufficiently smooth domain $\Omega \subset \mathbb{R}^d$ we now consider a pure diffusion system of the form

$$\dot{\boldsymbol{n}} = \operatorname{div}\Big(\widetilde{\mathbb{M}}(\boldsymbol{n})\nabla\boldsymbol{n}\Big) \text{ for } x \in \Omega, \quad \mathbb{M}(\boldsymbol{n})\nabla\boldsymbol{n}\cdot\nu = 0 \text{ on } \partial\Omega.$$

Here $\nabla\boldsymbol{n} \in \mathbb{R}^{I\times d}$ and $\widetilde{\mathbb{M}}(\boldsymbol{n}) \in \mathrm{Lin}(\mathbb{R}^{I\times d};\mathbb{R}^{I\times d})$. We will see that $\widetilde{\mathbb{M}}$ must have a certain structure to allow for a gradient structure with respect to the same free energy as above, namely $\mathcal{F}(\boldsymbol{n}) = \int_\Omega F(\boldsymbol{n}(x))\,\mathrm{d}x$ where $F(\boldsymbol{n}) = \sum_{i=1}^I n_i(\log n_i - 1)$.

The dual dissipation functional is

$$\Psi_{\text{diff}}^*(\boldsymbol{n}, \boldsymbol{\mu}) = \int_\Omega \nabla\boldsymbol{\mu}\cdot\mathbb{M}(\boldsymbol{n})\nabla\boldsymbol{\mu}\,\mathrm{d}x,$$

where $\mathbb{M}(\boldsymbol{n}) \in \mathrm{Lin}(\mathbb{R}^{I\times d};\mathbb{R}^{I\times d})$ is assumed to be symmetric and positive semi-definite. Using $\boldsymbol{\mu} = \mathrm{D}F(\boldsymbol{n}) = (\log n_i)_{i=1,\ldots,I}$ leads to the dual gradient flow

$$\dot{\boldsymbol{n}} = \mathrm{D}_{\boldsymbol{\mu}}\Psi_{\text{diff}}^*(\boldsymbol{n}, -\mathrm{D}F(\boldsymbol{n})) = \operatorname{div}\big(\mathbb{M}(\boldsymbol{n})\boldsymbol{D}_{\boldsymbol{n}}^{-1}\nabla\boldsymbol{n}\big) \text{ with } \boldsymbol{D}_{\boldsymbol{n}} := \operatorname{diag}(n_1, ..., n_I).$$

Thus, we reveal the special form needed for $\widetilde{\mathbb{M}}(\boldsymbol{n})$, namely

$$\widetilde{\mathbb{M}}(\boldsymbol{n}) = \mathbb{M}(\boldsymbol{n})\boldsymbol{D}_{\boldsymbol{n}}^{-1}, \text{ where } \boldsymbol{D}_{\boldsymbol{n}}^{-1} = \mathrm{D}^2F(\boldsymbol{n}).$$

The situation is simple, if there is no cross-diffusion, i.e.

$$\operatorname{div}\big(\widetilde{\mathbb{M}}(\boldsymbol{n})\nabla\boldsymbol{n}\big) = \Big(\operatorname{div}\big(\widetilde{M_i}(\boldsymbol{n})\nabla n_i\big)\Big)_{i=1,\ldots,I} \text{ with } \widetilde{M_i}(\boldsymbol{n}) \in \mathbb{R}^{d\times}_{\text{spsd}}.$$

Then, we let $\nabla\boldsymbol{\mu}\cdot\mathbb{M}(\boldsymbol{n})\nabla\boldsymbol{\mu} = \sum_{i=1}^{I} n_i\nabla\mu_i\cdot\widetilde{M}_i(\boldsymbol{n})\nabla\mu_i$, which leads to a sum of scalar Wasserstein metrics for each components, if the matrices $\widetilde{M}_i$ are constant. In particular, it is easy to obtain the diagonal system

$$\dot{\boldsymbol{n}} = \mathrm{diag}(\widetilde{M}_1,\ldots,\widetilde{M}_I)\Delta\boldsymbol{n}$$

However, for systems with cross-diffusion the situation is more complicated, since unsymmetries and nontrivial dependencies on $\boldsymbol{n}$ will appear.

The gradient structure is obtained from the metric induced by Ψ^*_{diff} via Legendre transform. For this we use mass conservation $\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega \boldsymbol{n}(t,x)\,\mathrm{d}x \equiv 0$ and define $X_{00} = \{\, \boldsymbol{v} \in \mathrm{L}^2(\Omega;\mathbb{R}^I) \mid \int_\Omega \boldsymbol{v}(x)\,\mathrm{d}x = 0 \,\}$. On the formal level we obtain, for $\boldsymbol{v}\in X_{00}$, the formula

$$\Psi_{\mathrm{diff}}(\boldsymbol{n},\boldsymbol{v}) = \int_\Omega \frac{1}{2}\boldsymbol{v}\cdot\mathcal{M}_{\boldsymbol{n}}^{-1}\boldsymbol{v}\,\mathrm{d}x = \int_\Omega \frac{1}{2}\boldsymbol{v}\cdot\boldsymbol{\mu}_{\boldsymbol{n}}^{\boldsymbol{v}}\,\mathrm{d}x = \int_\Omega \frac{1}{2}\nabla\boldsymbol{\mu}_{\boldsymbol{n}}^{\boldsymbol{v}}\cdot\mathbb{M}(\boldsymbol{n})\nabla\boldsymbol{\mu}_{\boldsymbol{n}}^{\boldsymbol{v}}\,\mathrm{d}x, \tag{3.4}$$

where $\boldsymbol{\mu}_{\boldsymbol{n}}^{\boldsymbol{v}}$ is the unique solution in X_{00} of

$$\boldsymbol{v} = \mathcal{M}_{\boldsymbol{n}}\boldsymbol{\mu} = -\,\mathrm{div}(\mathbb{M}(\boldsymbol{n})\nabla\boldsymbol{\mu}) \text{ in } \Omega, \quad (\mathbb{M}(\boldsymbol{n})\nabla\boldsymbol{\mu})\cdot\nu = 0 \text{ on } \partial\Omega.$$

Thus, we have found the formal gradient system

$$0 = \mathrm{D}_{\dot{\boldsymbol{n}}}\Psi_{\mathrm{diff}}(\boldsymbol{n},\dot{\boldsymbol{n}}) + \mathrm{D}\mathcal{F}(\boldsymbol{n}) \iff \dot{\boldsymbol{n}} = \mathrm{D}\Psi^*_{\mathrm{diff}}(\boldsymbol{n},-\mathrm{D}\mathcal{F}(\boldsymbol{n})).$$

3.3 Combining reactions and diffusion

Combining reactions and diffusion is simple in the rate form, since we just have to add the dual dissipation potentials, because we have the same driving functional $\mathcal{F}$ in both cases. For the given domain $\Omega\subset\mathbb{R}^d$ we define the underlying space $X = \mathrm{L}^1(\Omega;\mathbb{R}^I)$ and the functionals

$$\mathcal{F}(\boldsymbol{n}) = \int_\Omega F(\boldsymbol{n}(x))\,\mathrm{d}x \text{ with } F(\boldsymbol{n}) = \sum_{i=1}^{I} n_i(\log n_i - 1),$$
$$\Psi^*(\boldsymbol{n},\boldsymbol{\mu}) = \int_\Omega \frac{1}{2}\nabla\boldsymbol{\mu}(x)\cdot(\mathbb{M}(\boldsymbol{n}(x))\nabla\boldsymbol{\mu}(x)) + \psi^*(\boldsymbol{n}(x),\boldsymbol{\mu}(x))\,\mathrm{d}x.$$

with ψ^* for Section 3.1.

To make the structure more exact, we need to employ the conserved quantities. We define the subspace

$$X_0 := \{\, \boldsymbol{n}\in X \mid \int_\Omega \boldsymbol{n}(x)\,\mathrm{d}x \in \mathbb{S} \,\},$$

and the conserved quantities $\mathcal{C}_{\boldsymbol{\xi}}(\boldsymbol{n}) = \int_\Omega \boldsymbol{n}(x)\cdot\boldsymbol{\xi}\,\mathrm{d}x$, where $\boldsymbol{\xi}\in\mathbb{S}^\perp$. For simplicity we now assume that $k^r(\boldsymbol{n}) > 0$ and $\mathbb{M}(\boldsymbol{n})$ are positive definite for all $\boldsymbol{n}\in\,]0,\infty[^I$. Then, the kernel of the quadratic form $\Psi^*(\boldsymbol{n},\cdot)$ can be characterized easily. The diffusive term gives $\nabla\boldsymbol{\mu}\equiv 0$ and the reaction part ψ^* gives $\boldsymbol{\mu}(x)\in\mathbb{S}^\perp$ a.e. Thus the kernel is exactly the orthogonal complement of X_0, namely

$$X_0^\perp = \{\, \boldsymbol{\mu}\in\mathrm{L}^2(\Omega;\mathbb{R}^I) \mid \exists\,\boldsymbol{\xi}\in\mathbb{S}^\perp:\ \boldsymbol{\mu}(x) = \boldsymbol{\xi} \text{ a.e.} \,\}.$$

Thus, we are able to define $\Psi(\boldsymbol{n},\cdot)$ as formal metric via the Legendre transform of Ψ^*. For $\boldsymbol{v}\in X_0$ we let

$$\Psi(\boldsymbol{n},\boldsymbol{v}) = \int_\Omega \frac{1}{2}\boldsymbol{v}\cdot\mathcal{A}_{\boldsymbol{n}}^{-1}\boldsymbol{v}\,\mathrm{d}x = \int_\Omega \frac{1}{2}\boldsymbol{v}\cdot\widetilde{\boldsymbol{\mu}}_{\boldsymbol{n}}^{\boldsymbol{v}}\,\mathrm{d}x = \Psi^*(\boldsymbol{n},\widetilde{\boldsymbol{\mu}}_{\boldsymbol{n}}^{\boldsymbol{v}}),$$

where $\widetilde{\boldsymbol{\mu}}_{\boldsymbol{n}}^{\boldsymbol{v}}$ is the unique solution in X_0 of

$$\boldsymbol{v} = \mathcal{A}_{\boldsymbol{n}}\widetilde{\boldsymbol{\mu}} = -\operatorname{div}(\mathbb{M}(\boldsymbol{n})\nabla\widetilde{\boldsymbol{\mu}}) + \boldsymbol{H}(\boldsymbol{n})\widetilde{\boldsymbol{\mu}} \text{ in } \Omega, \quad (\mathbb{M}(\boldsymbol{n})\nabla\boldsymbol{\mu})\cdot\nu = 0 \text{ on } \partial\Omega.$$

Since Ψ^* has the additive form $\Psi^*_{\text{diff}}+\Psi^*_{\text{react}}$ with $\Psi^*_{\text{react}}(\boldsymbol{n},\boldsymbol{\mu}) = \int_\Omega \psi^*(\boldsymbol{n}(x),\boldsymbol{\mu}(x))\,\mathrm{d}x$ its Legendre transform can also be obtained via the inf-convolution, namely

$$\Psi(\boldsymbol{n},\boldsymbol{v}) = \inf\{\,\Psi_{\text{diff}}(\boldsymbol{n},\boldsymbol{v}_1)+\Psi_{\text{react}}(\boldsymbol{n},\boldsymbol{v}_2)\mid \boldsymbol{v}_1+\boldsymbol{v}_2=\boldsymbol{v}\,\}$$

where Ψ_{diff} is defined in (3.4) while Ψ_{react} is obtained from ψ in (3.3) via integration over Ω. Altogether, we have established the gradient form

$$0 = \mathrm{D}_{\dot{\boldsymbol{n}}}\Psi(\boldsymbol{n},\dot{\boldsymbol{n}}) + \mathrm{D}\mathcal{F}(\boldsymbol{n}).$$

3.4 An example of reversible reaction-diffusion systems

To highlight the structures we give an elementary example, where the diffusion part is constant, isotropic, and without cross-diffusion. The system has two species X_1 and X_2 with the single reversible reaction $pX_1 \rightleftharpoons qX_2$. The reaction-diffusion system

$$\dot{n}_1 = M_1\Delta n_1 - kp(n_1^p - n_2^q), \quad \dot{n}_2 = M_2\Delta n_2 + kq(n_1^p - n_2^q) \quad \text{in } \Omega, \tag{3.5}$$

which we complete with the no-flux boundary conditions $\nabla n_i\cdot\nu = 0$ on $\partial\Omega$. For the special case $p=q=1$ the gradient structure was derived independently in [PSV09].

As given above, the free energy is $\mathcal{F}(n_1,n_2) = \int_\Omega n_1(\log n_1 - 1) + n_2(\log n_2 - 1)\,\mathrm{d}x$ and the dual dissipation potential is

$$\Psi^*(n_1,n_2;\mu_1,\mu_2) = \frac{1}{2}\int_\Omega n_1M_1|\nabla\mu_1|^2 + n_2M_2|\nabla\mu_2|^2 + k\ell(n_1^p,n_2^q)(p\mu_1 - q\mu_2)^2\,\mathrm{d}x,$$

where ℓ is given in (3.1). Obviously, $\mathbb{S}^\perp = \operatorname{span}\binom{q}{p}$ and $\mathcal{C}(n_1,n_2) = \int_\Omega qn_1 + pn_2\,\mathrm{d}x$ is a conserved quantity.

For the given initial value $(n_1(0),n_2(0))\in \mathrm{H}^1(\Omega;\mathbb{R}^2)$ the unique solution of (3.5) will converge to the unique steady state which is the minimizer of $\boldsymbol{n}\mapsto\mathcal{F}(\boldsymbol{n})$ subjected to the constraint $\mathcal{C}(\boldsymbol{n}) = \mathcal{C}(n_1(0),n_2(0))$, which is a spatially constant state.

3.5 Reaction-diffusion systems with temperature coupling

As next increase of complexity we also include temperature effects into the gradient structure. In this case we will use a functional for the energy conservation, while the entropy will take over role of the driving functional. To model temperature effects we have several choices for the the additional internal variable, namely the temperature, the internal energy, or the entropy, see [Mie10] for more details. To obtain our joint gradient structure it seems best to use the internal energy $u : \Omega \to \mathbb{R}$, which leads to the functionals

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

for the total energy and the total entropy, respectively. Hence, $S : \,]0, \infty[^I \times \mathbb{R} \to \mathbb{R}$ models the thermodynamic properties of the system. The corresponding thermodynamic driving forces are

$$\boldsymbol{\eta} = \mathrm{D}_{\boldsymbol{n}}\boldsymbol{\mathcal{S}}(\boldsymbol{n}, u) = \partial_{\boldsymbol{n}} S(\boldsymbol{n}, u), \quad \tau = \mathrm{D}_u \boldsymbol{\mathcal{S}}(\boldsymbol{n}, u) = \partial_u S(\boldsymbol{n}, u),$$

where, by standard thermodynamic modeling, $\theta = \frac{1}{\theta} > 0$ is the absolute temperature.

We define a dual potential Ψ^* for the driving forces $(\boldsymbol{\eta}, \tau)$ via

$$\Psi^*(\boldsymbol{n}, u; \boldsymbol{\eta}, \tau) = \int_\Omega \frac{1}{2} \nabla \begin{pmatrix} \boldsymbol{\eta} \\ \tau \end{pmatrix} \cdot M(\boldsymbol{n}, u) \nabla \begin{pmatrix} \boldsymbol{\eta} \\ \tau \end{pmatrix} + \psi^*(\boldsymbol{n}, u, \boldsymbol{\eta}) \,\mathrm{d}x,$$

where ψ^* is given as in Section 3.1, but now the reaction rates may depend on the temperature via the internal energy, i.e.

$$\psi^*(\boldsymbol{n}, u; \boldsymbol{\eta}) = \sum_{r=1}^R \frac{\widehat{k}^r(\boldsymbol{n}, u)}{2} \ell(\boldsymbol{n}^{\boldsymbol{\alpha}^r}, \boldsymbol{n}^{\boldsymbol{\beta}^r}) \big(\boldsymbol{\eta} \cdot (\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r)\big)^2 = \frac{1}{2} \boldsymbol{\eta} \cdot \widehat{\boldsymbol{H}}(\boldsymbol{n}, u) \boldsymbol{\eta}.$$

Here the coefficients $\widehat{k}^r$ are different from k^r in (3.1), since $\boldsymbol{\eta}$ has the physical dimension of $\boldsymbol{\mu}$ divided by temperature (e.g. we may take $\widehat{k}^r = \theta^2 k^r$). In particular, Ψ^* is now the dual entropy-production potential.

Using $\mathrm{D}\mathcal{E}(\boldsymbol{n}, u) = \binom{\boldsymbol{0}}{1}$, we easily find the invariance

$$\Psi^*(\boldsymbol{n}, u; \tbinom{\boldsymbol{\eta}}{\tau} + \lambda_1 \mathrm{D}\mathcal{E} + \lambda_2 \mathrm{D}\mathcal{C}_{\boldsymbol{\xi}}) = \Psi^*(\boldsymbol{n}, u, \boldsymbol{\eta}, \tau) \quad \text{for all } \lambda_1, \lambda_2 \in \mathbb{R},\ \boldsymbol{\xi} \in \mathbb{S}^\perp. \tag{3.6}$$

The dual gradient system $\binom{\dot{\boldsymbol{n}}}{\dot{u}} = \mathrm{D}_{(\boldsymbol{\eta}, \tau)} \Psi^*(\boldsymbol{n}, u; \mathrm{D}\boldsymbol{\mathcal{S}}(\boldsymbol{n}, u))$ takes the form

$$\begin{aligned} \dot{\boldsymbol{n}} &= -\operatorname{div} \boldsymbol{j}_{\boldsymbol{n}} + \widehat{\boldsymbol{H}}(\boldsymbol{n}, u) \partial_{\boldsymbol{n}} S(\boldsymbol{n}, u), \\ \dot{u} &= -\operatorname{div} j_u, \end{aligned} \qquad \begin{pmatrix} \boldsymbol{j}_{\boldsymbol{n}} \\ j_u \end{pmatrix} = M(\boldsymbol{n}, u) \begin{pmatrix} \nabla \partial_{\boldsymbol{n}} S(\boldsymbol{n}, u) \\ \nabla \partial_u S(\boldsymbol{n}, u) \end{pmatrix}. \tag{3.7}$$

Using the no-flux boundary conditions it is easy to see that the total energy $\mathcal{E}$ as well as all $\mathcal{C}_{\boldsymbol{\xi}}$ are conserved along solutions.

However, it is more common to use the temperature θ instead of the internal energy u. Thus, based on the free energy $\overline{F}(\boldsymbol{n}, \theta)$ we may define the relations

$$u = \overline{U}(\boldsymbol{n}, \theta) := \overline{F}(\boldsymbol{n}, \theta) - \theta \partial_\theta \overline{F}(\boldsymbol{n}, \theta), \quad s = \overline{S}(\boldsymbol{n}, \theta) := -\partial_\theta \overline{F}(\boldsymbol{n}, \theta). \tag{3.8}$$

We arrive at the functionals

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

Using the abstract transformation rule in Remark 2.1, we obtain the transformed $\overline{\Psi}^*$ via

$$\overline{\Psi}^*(\boldsymbol{n},\theta;\boldsymbol{\mu}_{\boldsymbol{n}},\mu_\theta) = \Psi^*(\boldsymbol{n},\overline{U}(\boldsymbol{n},\theta);\boldsymbol{\mu}_{\boldsymbol{n}} - \frac{\mu_\theta}{\partial_\theta\overline{U}(\boldsymbol{n},\theta)}\partial_{\boldsymbol{n}}\overline{U}(\boldsymbol{n},\theta), \frac{\mu_\theta}{\partial_\theta\overline{U}(\boldsymbol{n},\theta)}).$$

Thus, (3.7) is equivalent to a dual gradient system for $(\boldsymbol{n},\theta)$ in the form

$$\binom{\dot{\boldsymbol{n}}}{\dot{\theta}} = \mathrm{D}\overline{\Psi}^*(\boldsymbol{n},\theta,\mathrm{D}_{\boldsymbol{n}}\overline{\mathcal{S}}(\boldsymbol{n},\theta),\mathrm{D}_\theta\overline{\mathcal{S}}(\boldsymbol{n},\theta)).$$

Again we have conservation of energy via $\Psi^*(\boldsymbol{n},\theta;(\boldsymbol{\eta},\mu_\theta)+\lambda\mathrm{D}_{\boldsymbol{n},\theta}\overline{\mathcal{E}}) = \Psi^*(\boldsymbol{n},\theta;\boldsymbol{\eta},\mu_\theta)$. Moreover, using the definition of $\overline{U}$ and $\overline{S}$ via $\overline{F}$ in (3.8) we obtain

$$\begin{aligned}
&\partial_{\boldsymbol{n}}\overline{S} - \frac{\partial_\theta\overline{S}}{\partial_\theta\overline{U}}\partial_{\boldsymbol{n}}\overline{U} = -\frac{1}{\theta}\partial_{\boldsymbol{n}}\overline{F}, \quad \frac{\partial_\theta\overline{S}}{\partial_\theta\overline{U}} = \frac{1}{\theta},\\
&\overline{\Psi}^*(\boldsymbol{n},\theta;\mathrm{D}_{\boldsymbol{n}}\overline{\mathcal{S}}(\boldsymbol{n},\theta),\mathrm{D}_\theta\overline{\mathcal{S}}(\boldsymbol{n},\theta)) = \Psi^*(\boldsymbol{n},\overline{U}(\boldsymbol{n},\theta);\frac{1}{\theta}\partial_{\boldsymbol{n}}\overline{F}(\boldsymbol{n},\theta),\frac{1}{\theta}).
\end{aligned}$$

This leads to a coupled system for $(\boldsymbol{n},\theta)$ in the form

$$\begin{aligned}
&\dot{\boldsymbol{n}} = -\operatorname{div}\boldsymbol{j}_{\boldsymbol{n}} - \frac{1}{\theta}\overline{\boldsymbol{H}}(\boldsymbol{n},\theta)\partial_{\boldsymbol{n}}\overline{F}(\boldsymbol{n},\theta),\\
&\dot{\theta} = \frac{1}{\partial_\theta\overline{U}}\Big(-\operatorname{div} j_\theta + \partial_{\boldsymbol{n}}\overline{U}\cdot\operatorname{div}\boldsymbol{j}_{\boldsymbol{n}} + \frac{1}{\theta}\partial_{\boldsymbol{n}}\overline{U}\cdot\overline{\boldsymbol{H}}(\boldsymbol{n},\theta)\partial_{\boldsymbol{n}}\overline{F}(\boldsymbol{n},\theta)\Big),\\
&\text{where } \overline{H}(\boldsymbol{n},\theta) = \widehat{\boldsymbol{H}}(\boldsymbol{n},\overline{U}(\boldsymbol{n},\theta)) \text{ and } \begin{pmatrix}\boldsymbol{j}_{\boldsymbol{n}}\\ j\theta\end{pmatrix} = M(\boldsymbol{n},\overline{U}(\boldsymbol{n},\theta))\nabla\begin{pmatrix}-\frac{1}{\theta}\partial_{\boldsymbol{n}}\overline{F}\\ \frac{1}{\theta}\end{pmatrix}.
\end{aligned}\tag{3.9}$$

In this system we clearly see the influence of reactions on the temperature and vice versa. Moreover, the above derivation shows that (3.9) is a gradient system for the driving functional $-\overline{\mathcal{S}}$ and the dual potential $\overline{\Psi}^*$, which keeps $\overline{\mathcal{E}}$ invariant.

To see a little more the structure of the equations we consider a free energy in the form

$$\overline{F}(\boldsymbol{n},\theta) = c\theta(1-\log\theta) + F_0(\boldsymbol{n}) + \theta F_1(\boldsymbol{n}).$$

For the internal energy and the entropy we obtain

$$\overline{U}(\boldsymbol{n},\theta) = c\theta + F_0(\boldsymbol{n}), \quad \overline{S}(\boldsymbol{n},\theta) = c\log\theta - F_1(\boldsymbol{n}).$$

Typically $F_1(\boldsymbol{n}) = \sum_{i=1}^I f_i(n_i)$ with convex f_i (e.g. $f_i(n) = n(\log n-1)$), which makes $\overline{S}$ concave. A particularly simple case is obtained if $F_0 \equiv 0$, because now $\overline{U}$ depends only on θ and $\frac{1}{\theta}\partial_{\boldsymbol{n}}\overline{F}$ is independent of θ. Then, we obtain a weakly coupled system only, namely

$$\begin{aligned}
&\dot{\boldsymbol{n}} = \operatorname{div}\big(M_{\boldsymbol{nn}}(\boldsymbol{n},\theta)\nabla\partial_{\boldsymbol{n}}F_1(\boldsymbol{n})\big) - \widehat{\boldsymbol{H}}(\boldsymbol{n},\theta)\partial_{\boldsymbol{n}}F_1(\boldsymbol{n}),\\
&\dot{\theta} = -\operatorname{div}\big(M_{\theta\theta}(\boldsymbol{n},\theta)\nabla(1/\theta)\big).
\end{aligned}$$

We may simplify further by assuming $M_{\theta\theta}(\boldsymbol{n},\theta) = \theta I$, then the last equation is the linear heat equation.

4 Semiconductor equations

The additional feature in semiconductors, or more generally in electro-reaction-diffusion systems, is that we need to take into account the electric charges of the species. These charges generate an electrostatic potential whose electric field creates drift forces proportional to the charges of the species. Thus, the flux terms are now given in terms of drift and diffusion. That is why these systems are also called (energy)-drift-diffusion equations, see [Gaj94, AGH02, Gli08, GlG09].

As an easy start, in Section 4.1, we treat the simplest semiconductor model, namely the van Roosbroeck system. This system has two species, namely electrons and holes with densities n and p, respectively. The single reaction is called 'recombination', since an electron-hole pair can be created or annihilated. In Section 4.2 we show that general electro-reaction-diffusion systems with arbitrary charge distributions and with temperature effects can be written with a dual gradient structure. As before, the main assumption is that the reactions or recombinations are strongly reversible or satisfy the detailed balance condition, see Remark 3.1. In particular, we conclude that all systems treated in [AGH02] have a dual gradient structure.

4.1 The van Roosbroeck system with recombination

Here we treat the simplest isothermal model, where total energy is the driving functional. For simplicity and clarity of the concept, we set most material parameters equal to 1. For the general case, we refer to the next subsection, where general materials and many species are treated.

The state of the system is described by the densities n and p of electrons and holes, respectively. A density $\boldsymbol{n} = (n, p) : \Omega \to]0, \infty[^2$ generates an electrostatic potential $\phi_{\boldsymbol{n}}$ as the unique solution of the linear potential equation

$$-\Delta\phi = \delta - n + p \text{ in } \Omega, \qquad \phi = \phi_{\mathrm{Dir}} \text{ on } \partial\Omega, \tag{4.1a}$$

where $\delta : \Omega \to \mathbb{R}$ a given doping profile. The different sign in front of n and p reflect the different charge of electrons and holes, respectively. The evolution of the densities (n, p) is governed by diffusion, drift according to $\nabla\phi_{\boldsymbol{n}}$, and recombination according to the simple creation-annihilation reaction for electron-hole pairs, viz.,

$$X_n + X_p \rightleftharpoons 0, \quad \text{i.e. } \alpha = \binom{1}{1} \text{ and } \beta = \binom{0}{0}.$$

Since the material parameters are all 1, the drift-diffusion system reads

$$\begin{aligned} \dot{n} &= \operatorname{div}\big(\nabla n - n\,\nabla\phi_{\boldsymbol{n}}\big) - (np{-}1), \\ \dot{p} &= \operatorname{div}\big(\nabla p + p\,\nabla\phi_{\boldsymbol{n}}\big) - (np{-}1). \end{aligned} \tag{4.1b}$$

Note that the fluxes $j_n = \nabla n - n\nabla\phi_{\boldsymbol{n}}$ and $j_p = \nabla p + p\nabla\phi_{\boldsymbol{n}}$ include the diffusive parts due to ∇n or ∇p (Fick's law) as well as the charge-dependent drift parts $-n\nabla\phi_{\boldsymbol{n}}$ and $+p\nabla\phi_{\boldsymbol{n}}$.

For establishing a gradient structure we define the functionals $\mathcal{E}$ and $\mathcal{Q}$ as the total energy (sum of electrostatic and free energy) and the total charge, respectively:

$$\mathcal{E}(\boldsymbol{n}) = \int_\Omega \frac{1}{2}|\nabla\phi_{\boldsymbol{n}}|^2 + F(n,p)\,\mathrm{d}x \quad\text{and}\quad \mathcal{Q}(\boldsymbol{n}) = \int_\Omega \delta{-}n{+}p\,\mathrm{d}x,$$

where $F(n,p) = n(\log n{-}1) + p(\log p{-}1)$. The differentials read

$$\mathrm{D}\mathcal{E}(\boldsymbol{n}) = \begin{pmatrix}\log n - \phi_{\boldsymbol{n}}\\ \log p + \phi_{\boldsymbol{n}}\end{pmatrix} \quad\text{and}\quad \mathrm{D}\mathcal{Q}(\boldsymbol{n}) = \begin{pmatrix}-1\\ 1\end{pmatrix}.$$

For the first relation one needs to use that $\phi_{\boldsymbol{n}}$ solves (4.1a) and depends linearly on $\boldsymbol{n}$, see [AGH02, Lem. 6.1]. The dual dissipation potential is chosen as

$$\Psi^*(n,p;\mu_n,\mu_p) = \int_\Omega \frac{n}{2}|\nabla\mu_n|^2 + \frac{p}{2}|\nabla\mu_p|^2 + \frac{\ell(np,1)}{2}(\mu_n{+}\mu_p)^2\,\mathrm{d}x,$$

where ℓ is defined in (3.1). Thus, we again have two Wasserstein terms for the mobilities plus a reaction term.

We immediately find $\Psi^*(\boldsymbol{n};\boldsymbol{\mu}{+}\lambda\mathrm{D}\mathcal{Q}(\boldsymbol{n})) = \Psi^*(\boldsymbol{n};\boldsymbol{\mu})$ for all $\lambda\in\mathbb{R}$. Moreover, using

$$\Psi^*(\boldsymbol{n};-\mathrm{D}\mathcal{E}(\boldsymbol{n})) = \begin{pmatrix}-\operatorname{div}\big(n\nabla(-\log n + \phi_{\boldsymbol{n}})\big) + \ell(np,1)(-\log(np))\\ -\operatorname{div}\big(p\nabla(-\log p - \phi_{\boldsymbol{n}})\big) + \ell(np,1)(-\log(np))\end{pmatrix}$$

we see that $\dot{\boldsymbol{n}} = \Psi^*(\boldsymbol{n};-\mathrm{D}\mathcal{E}(\boldsymbol{n}))$ is the desired dual gradient structure of the van Roosbroeck system (4.1).

4.2 Energy-drift-diffusion equations with recombination

We now follow the general setup for semiconductor models with temperature developed in [AGH02]. The vector $\boldsymbol{n} = (n_1,\dots,n_I):\Omega\to\mathbb{R}^I$ contains all densities, where $i = 1,\dots,I$ labels the different species, such as electrons, holes, ions, excited states, traps, etc. Each species is assumed to have a charge number, which are collected in the charge vector $\boldsymbol{q} = (q_1,\dots,q_I)\in\mathbb{Z}^I$. To include the energy properly, we use the internal energy u.

According to [AGH02, Thm. 6.2 and Rem. 7.3], the balance equations take the form

$$\dot{\boldsymbol{n}} + \operatorname{div}\boldsymbol{j}_{\boldsymbol{n}} = \boldsymbol{R} \quad \text{in } \Omega, \quad \boldsymbol{j}_{\boldsymbol{n}}\cdot\nu = 0 \text{ on } \partial\Omega; \tag{4.2a}$$

$$\dot{u} + \operatorname{div} j_u = \phi\boldsymbol{q}\cdot\operatorname{div}\boldsymbol{j}_{\boldsymbol{n}} \quad \text{in } \Omega, \quad j_u\cdot\nu = 0 \text{ on } \partial\Omega; \tag{4.2b}$$

$$-\operatorname{div}(\varepsilon\nabla\phi) = \delta + \boldsymbol{q}\cdot\boldsymbol{n} \quad \text{in } \Omega, \quad \phi = \phi_{\mathrm{Dir}} \text{ on } \Gamma_{\mathrm{Dir}} \text{ and } \varepsilon\nabla\phi\cdot\nu = 0 \text{ on } \Gamma_{\mathrm{Neu}}. \tag{4.2c}$$

Here δ is a doping profile, ϕ is the electrostatic potential, and $\varepsilon > 0$ is the electric permittivity (tensor). For the fluxes one now takes the ansatz

$$\begin{pmatrix}\boldsymbol{j}_{\boldsymbol{n}}\\ j_u\end{pmatrix} = M(\boldsymbol{n},u)\nabla\begin{pmatrix}\widetilde{\boldsymbol{\eta}}\\ \tau\end{pmatrix}, \tag{4.3}$$

where the mobility tensor M is assumed to be symmetric and positive semidefinite. (In case of immobile species, some entries of M should be ∞, in the sense that the corresponding quadratic form is only defined on a strict subspace.) As before, $(\widetilde{\boldsymbol{\eta}},\tau)$ will be suitable thermodynamic driving forces associated with $(\boldsymbol{n}, u)$ obtained from the entropy functional. As before, the recombination terms $\boldsymbol{R}$ will be given in the form

$$\boldsymbol{R}(\boldsymbol{n}, u) = \boldsymbol{H}(\boldsymbol{n}, u)\boldsymbol{\eta}, \tag{4.4}$$

where $\boldsymbol{H}$ is obtained from a general set of R strongly reversible reactions

$$\alpha_1^r X_i + \cdots \alpha_I^r X_I \rightleftharpoons \beta_1^r X_i + \cdots \beta_I^r X_I, \qquad r = 1, \ldots, R.$$

(As explained in Remark 3.1 it would be sufficient to have reactions satisfying the detailed balance condition and renormalizing the densities suitably.) We define the dual reaction potential

$$\psi^*(\boldsymbol{n}, u; \boldsymbol{\eta}) = \sum_{r=1}^{R} \frac{K_r(\boldsymbol{n}, u)}{2} \Big((\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r) \cdot \boldsymbol{\eta} \Big)^2 = \frac{1}{2} \boldsymbol{\eta} \cdot \boldsymbol{H}(\boldsymbol{n}, u)\boldsymbol{\eta}.$$

Note that we have subsumed the previous product $k^r(\boldsymbol{n}, u)\ell(\boldsymbol{n}^{\alpha^r}, \boldsymbol{n}^{\beta^r})$ into one constant $K_r(\boldsymbol{n}, u)$. This generalizes the approach and allows for the usage of Fermi-Dirac statistics instead of the Boltzmann statistics only. However, we will lose the polynomial form of the reaction terms $\boldsymbol{R}$, see Remark 4.2.

The important point in electro-chemical reactions is that each reaction preserves the total amount of electric charge. Using the stoichiometric subspace $\mathbb{S} \subset \mathbb{R}^I$ introduced in (3.2) and its orthogonal complement $\mathbb{S}^\perp$, this simply means $\boldsymbol{q} \in \mathbb{S}^\perp$. Hence, ψ^* satisfies the invariance $\psi^*(\boldsymbol{n}, u; \boldsymbol{\eta} + \lambda \boldsymbol{q}) = \psi^*(\boldsymbol{n}, u; \boldsymbol{\eta})$ for all $\lambda \in \mathbb{R}$, which implies $\boldsymbol{R}(\boldsymbol{n}, u) \cdot \boldsymbol{q} \equiv 0$.

To describe the full gradient structure, we introduce the functionals for the total charge, the total energy, and the entropy via

$$\mathcal{Q}(\boldsymbol{n}, u) = \int_\Omega \delta + \boldsymbol{q} \cdot \boldsymbol{n} \,\mathrm{d}x, \quad \mathcal{E}(\boldsymbol{n}, u) = \int_\Omega \frac{1}{2} \nabla \phi_{\boldsymbol{n}} \cdot \varepsilon \nabla \phi_{\boldsymbol{n}} + u \,\mathrm{d}x, \quad \mathcal{S}(\boldsymbol{n}, u) = \int_\Omega S(\boldsymbol{n}, u) \,\mathrm{d}x,$$

respectively, where $\phi_{\boldsymbol{n}}$ is the unique solution of the Poisson equation (4.2c). The entropy density $S(\boldsymbol{n}, u)$ encodes the material properties in dependence on the temperature, but now expressed in terms of the internal energy. In [AGH02, Prop. 3.2] it is shown that it is physically reasonable (for certain semiconductor materials) to assume that $S :]0, \infty[^I \times \mathbb{R} \to \mathbb{R}$ is strictly concave.

For the differentials we obtain the expressions

$$\mathrm{D}\mathcal{Q}(\boldsymbol{n}, u) = \begin{pmatrix} \boldsymbol{q} \\ 0 \end{pmatrix}, \quad \mathrm{D}\mathcal{E}(\boldsymbol{n}, u) = \begin{pmatrix} \phi_{\boldsymbol{n}} \\ 1 \end{pmatrix}, \quad \mathrm{D}\mathcal{S}(\boldsymbol{n}, u) = \begin{pmatrix} \boldsymbol{\eta} \\ \tau \end{pmatrix},$$

where $\tau = 1/\theta = \partial_u S(\boldsymbol{n}, u)$ is the inverse temperature and $\boldsymbol{\eta} = \partial_{\boldsymbol{n}} S(\boldsymbol{n}, u)$.

We first check that the semiconductor system (4.2) is thermodynamically consistent in the sense of [AGH02], viz. the total charge and the total energy are constant and the entropy grows along solutions. For this we still need to specify the thermodynamic driving force $\widetilde{\boldsymbol{\eta}}$ in the flux relation (4.3). We follow [AGH02] and let

$$\widetilde{\boldsymbol{\eta}} = \mathrm{D}_{\boldsymbol{n}} \mathcal{S}(\boldsymbol{n}, u) - \frac{1}{\theta} \mathrm{D}_{\boldsymbol{n}} \mathcal{E}(\boldsymbol{n}, u) = \partial_{\boldsymbol{n}} S(\boldsymbol{n}, u) - \partial_u S(\boldsymbol{n}, u) \phi_{\boldsymbol{n}} \boldsymbol{q}.$$

Charge conservation, energy conservation and entropy production for solutions of (4.2) is now obtained as follows:

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{Q}(\boldsymbol{n},u) &= \langle \mathrm{D}\mathcal{Q}(\boldsymbol{n},u),(\dot{\boldsymbol{n}},\dot{u})\rangle \\
&= \int_\Omega \boldsymbol{q}\cdot(\boldsymbol{R}-\operatorname{div}\boldsymbol{j_n})\,\mathrm{d}x = -\int_\Omega \operatorname{div}\boldsymbol{q}\cdot\boldsymbol{j_n}\,\mathrm{d}x = 0;\\
\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{E}(\boldsymbol{n},u) &= \langle \mathrm{D}\mathcal{E}(\boldsymbol{n},u),(\dot{\boldsymbol{n}},\dot{u})\rangle \\
&= \int_\Omega \phi_{\boldsymbol{n}}\boldsymbol{q}\cdot(\boldsymbol{R}-\operatorname{div}\boldsymbol{j_n}) - \operatorname{div} j_u + \phi_n\boldsymbol{q}\cdot\operatorname{div}\boldsymbol{j_n}\,\mathrm{d}x = -\int_\Omega \operatorname{div} j_u\,\mathrm{d}x = 0;\\
\frac{\mathrm{d}}{\mathrm{d}t}\mathcal{S}(\boldsymbol{n},u) &= \langle \mathrm{D}\mathcal{S}(\boldsymbol{n},u),(\dot{\boldsymbol{n}},\dot{u})\rangle = \int_\Omega \partial_{\boldsymbol{n}}S(\boldsymbol{n},u)\cdot\dot{\boldsymbol{n}} + \partial_u S(\boldsymbol{n},u)\dot{u}\,\mathrm{d}x\\
&= \int_\Omega \big(\widetilde{\boldsymbol{\eta}}+\frac{\phi_{\boldsymbol{n}}}{\theta}\boldsymbol{q}\big)\cdot(\boldsymbol{R}-\operatorname{div}\boldsymbol{j_n}) + \frac{1}{\theta}\big(-\operatorname{div} j_u + \phi_{\boldsymbol{n}}\boldsymbol{q}\cdot\operatorname{div}\boldsymbol{j_n}\big)\,\mathrm{d}x\\
&= \int_\Omega -\widetilde{\boldsymbol{\eta}}\cdot\operatorname{div}\boldsymbol{j_n} - \frac{\operatorname{div} j_u}{\theta} + \widetilde{\boldsymbol{\eta}}\cdot\boldsymbol{R}\,\mathrm{d}x \;=\; \int_\Omega -\operatorname{div} j_s+\sigma_\nabla+\sigma_{\boldsymbol{R}}\,\mathrm{d}x\\
\text{with } j_s = \widetilde{\boldsymbol{\eta}}\cdot\boldsymbol{j_n}+\frac{1}{\theta}\,j_u,&\quad \sigma_\nabla = \nabla\tbinom{\widetilde{\boldsymbol{\eta}}}{\tau}\cdot M\nabla\tbinom{\widetilde{\boldsymbol{\eta}}}{\tau} \geq 0, \quad \text{and } \sigma_{\boldsymbol{R}} = \widetilde{\boldsymbol{\eta}}\cdot\boldsymbol{R}\geq 0.
\end{aligned}$$

where we used $\boldsymbol{q}\cdot\boldsymbol{R}\equiv 0$ several times as well as the no-flux boundary conditions $\boldsymbol{j_n}\cdot\nu = 0$ and $j_u\cdot\nu = 0$, which also imply $j_s\cdot\nu = 0$ for the entropy flux j_s. The entropy production due to diffusion σ_∇ is nonnegative by the positive definiteness of M, and the entropy production $\sigma_{\boldsymbol{R}}$ of the reaction terms is nonnegative because of (4.4) and $\boldsymbol{q}\cdot\boldsymbol{R}\equiv 0$ giving

$$\sigma_{\boldsymbol{R}} = \widetilde{\boldsymbol{\eta}}\cdot\boldsymbol{R}(\boldsymbol{n},u) = \boldsymbol{\eta}\cdot\boldsymbol{H}(\boldsymbol{n},u)\boldsymbol{\eta}\geq 0,$$

Finally we give the full dual gradient structure by defining the dual entropy-production potential Ψ^*. The point is that we need to use the modified driving force $\widetilde{\boldsymbol{\eta}}$ in the mobility term while we have to use the $\boldsymbol{\eta}$ in the reaction term:

$$\Psi^*(\boldsymbol{n},u;\boldsymbol{\eta},\tau) = \int_\Omega \frac{1}{2}\nabla\begin{pmatrix}\boldsymbol{\eta}-\tau\phi_{\boldsymbol{n}}\boldsymbol{q}\\ \tau\end{pmatrix}\cdot M(\boldsymbol{n},u)\nabla\begin{pmatrix}\boldsymbol{\eta}-\tau\phi_{\boldsymbol{n}}\boldsymbol{q}\\ \tau\end{pmatrix} + \psi^*(\boldsymbol{n},u,\boldsymbol{\eta})\,\mathrm{d}x. \tag{4.5}$$

The usage of $\widetilde{\boldsymbol{\eta}}$ in the mobility term serves a threefold purpose. First, it introduces the drift term into the balance equation for n, since (4.3) gives

$$\begin{pmatrix}\boldsymbol{j_n}\\ j_u\end{pmatrix} = M(\boldsymbol{n},u)\nabla\begin{pmatrix}\widetilde{\boldsymbol{\eta}}\\ \tau\end{pmatrix} = M(\boldsymbol{n},u)\begin{pmatrix}\nabla(\partial_{\boldsymbol{n}}S(\boldsymbol{n},u)-\frac{\phi_n}{\theta}\boldsymbol{q})\\ \nabla(1/\theta)\end{pmatrix}.$$

Second, charge and energy conservation are obtained from the invariance

$$\Psi^*(\boldsymbol{n},u;(\boldsymbol{\eta},\tau)+\lambda_1\mathrm{D}\mathcal{Q}(\boldsymbol{n},u)+\lambda_2\mathrm{D}\mathcal{E}(\boldsymbol{n},u)) = \Psi^*(\boldsymbol{n},u;\boldsymbol{\eta},\tau) \text{ for all } \lambda_1,\lambda_2\in\mathbb{R}.$$

Third, it produces the source term $\phi_{\boldsymbol{n}}\boldsymbol{q}\cdot\operatorname{div}\boldsymbol{j_n}$ in the the energy balance.

The latter statement and the derivation of the differential equation generated by the dual gradient system $\frac{\mathrm{d}}{\mathrm{d}t}\binom{\boldsymbol{n}}{u} = \mathrm{D}_{(\boldsymbol{\eta},\tau)}\Psi^*(\boldsymbol{n},u,\mathrm{D}\mathcal{S}(\boldsymbol{n},u))$ are obtained by noting the relation

$$\langle(\widehat{\boldsymbol{\eta}},\widehat{\tau}),\mathrm{D}\Psi^*(\boldsymbol{n},u;\mathrm{D}\mathcal{S}(\boldsymbol{n},u))\rangle = \int_\Omega \nabla\begin{pmatrix}\widehat{\boldsymbol{\eta}}-\widehat{\tau}\frac{\phi_n}{\theta}\boldsymbol{q}\\ \widehat{\tau}\end{pmatrix}\cdot\begin{pmatrix}\boldsymbol{j_n}\\ j_u\end{pmatrix} + \widehat{\boldsymbol{\eta}}\cdot\boldsymbol{H}(\boldsymbol{n},u)\partial_{\boldsymbol{n}}S(\boldsymbol{n},u)\,\mathrm{d}x,$$

which holds for all $(\widehat{\boldsymbol{\eta}}, \widehat{\tau})$. Comparing with $\langle(\widehat{\boldsymbol{\eta}}, \widehat{\tau}), (\dot{\boldsymbol{n}}, \dot{u})\rangle$ we easily obtain the equations

$$\dot{\boldsymbol{n}} = -\operatorname{div} \boldsymbol{j}_{\boldsymbol{n}} + \boldsymbol{H}(\boldsymbol{n}, u)\partial_{\boldsymbol{n}} S(\boldsymbol{n}, u)), \quad \dot{u} = -\operatorname{div} j_u + \phi_{\boldsymbol{n}} \boldsymbol{q} \cdot \operatorname{div} \boldsymbol{j}_{\boldsymbol{n}},$$

which are the desired equations (4.2a) and (4.2b).

Remark 4.1 (Pair interactions) *In [AGH02] all considered reactions are pair interaction and they are written in the form* $\widetilde{k}^{ij}(\boldsymbol{n}, u)(\mathrm{e}^{q_j\eta_j - q_i\eta_i} - 1)\boldsymbol{\alpha}, .$ *Obviously, these terms can be rewritten in the linear form* $K^{ij}(\boldsymbol{n}, u)(q_j\eta_j - q_i\eta_i)$ *where* $K^{ij}(\boldsymbol{n}, u) = k^{ij}(\boldsymbol{n}, u)\ell(\mathrm{e}^{m_{ij}(\boldsymbol{n},u)}, 1)$ *with* $m_{ij} = q_j\partial_{n_i} S - q_i\partial_{n_i} S$.

Moreover, the presentation in [AGH02] is for $\boldsymbol{n} = (n_0, n_1, n_2)$ *with* $\boldsymbol{q} = (-1, -1, 1)$, *where* n_1 *and* n_2 *are the electron and hole densities, respectively. The three reactions are*

$$X_1 + X_2 \rightleftharpoons 0, \quad X_0 + X_2 \rightleftharpoons 0, \quad X_0 \rightleftharpoons X_1.$$

The reactions are given in terms of exponentials of the electrochemical potentials $\xi_i = -q_i\mu_i$. *This suggests to introduce a non-quadratic dual potential* $\widehat{\psi}^*$ *in the form*

$$\widehat{\psi}^*(\boldsymbol{n}, \theta; \boldsymbol{\mu}) = \varrho_0(\boldsymbol{n}, \theta)\Xi(\mu_1 + \mu_2) + \varrho_1(\boldsymbol{n}, \theta)\Xi(\mu_0 + \mu_2) + \varrho_2(\boldsymbol{n}, \theta)\Xi(\mu_1 - \mu_0),$$

where $\Xi(t) = \mathrm{e}^t - 1 - t$. *Hence* $\widehat{\psi}^*(\boldsymbol{n}, \theta; \cdot) : \mathbb{R}^3 \to [0, \infty[$ *is smooth, strictly convex, and satisfies* $\widehat{\psi}^*(\boldsymbol{n}, \theta; 0) = 0$. *Combining this with the diffusion terms to a dual functional* $\widehat{\Psi}^*$ *one can define a generalized gradient system in the sense of* (2.3).

Remark 4.2 (Fermi-Dirac statistics) *In semiconductor models it is often desirable to replace the Boltzmann statistics by the more accurate Fermi-Dirac statistics. In [AGH02, Eqn. (1)] the following form for the free energy* $\overline{F}$ *is suggested:*

$$\overline{F}(\boldsymbol{n}, \theta) = c\theta(1 - \log\theta) - \sum_{i=1}^{I} q_i n_i E_i(\theta) + \theta \sum_{i=1}^{I} s_i(\theta) f_i(n_i/s_i(\theta)),$$

where E_i *denotes suitable energy levels and* s_i *state densities, which depend on the temperature. Here the functions* f_i *give rise to the chemical potentials*

$$\mu_i = \frac{1}{\theta}\partial_{n_i}\overline{F}(\boldsymbol{n}, \theta) = f_i'(n_i/s_i(\theta)) - q_i E_i(\theta).$$

IN the Boltzmann case one assumes $f_i'(n) = \log n$ *and obtains* $f_i(n) = n(\log n - 1)$. *For a Fermi-Dirac statistics one uses the Fermi integrals*

$$\mathbb{F}_\gamma(\mu) = \frac{1}{\Gamma(\gamma+1)} \int_0^\infty \frac{\zeta^\gamma}{1 + \exp(\zeta - \mu)} \mathrm{d}\zeta,$$

where the index satisfies $\gamma > -1$. *Note that* $\mathbb{F}_\gamma(\mu) \approx \mathrm{e}^\mu$ *and* $\mathbb{F}_\gamma(\mu) \approx \mu^\gamma$ *for* $\mu \ll 0$ *and* $\mu \gg 0$, *respectively. For* f_i' *we now take the inverse of some* $\mathbb{F}_{\gamma-1}$ *and obtain* $f_i(n) = n\mathbb{F}_{\gamma-1}^{-1}(n) - \mathbb{F}_\gamma(\mathbb{F}_{\gamma-1}^{-1}(n))$.

The main difference in using the Fermi-Dirac statistics is that linear combinations of chemical potentials can no longer be written as products of the densities. This is a special property of the logarithm, which is associated to the Boltzmann statistics.

Thus, when using the Fermi-Dirac statistics the recombination terms should not be written as polynomials. To keep the gradient structure it is essential to keep linear combinations of the chemical potentials, i.e. the classical recombination term $np - n_\mathrm{i}^2$ *needs to be replaced by* $K(n, p)(f_n'(n) + f_p'(p) - 2\mu_\mathrm{i})$.

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