

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

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Abstract

In recent years the theory of the Wasserstein metric has opened up new treatments of diffusion equations as gradient systems, where the free energy or 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 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 Albinus *et al* (2002 *Nonlinearity* 15 367–83), which stimulated this work, have a gradient structure.

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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

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

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 seem 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 known that for large classes of reaction systems there exist (convex) Liapunov functions, namely the free energy or 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 this work is the thermodynamical models for semiconductors derived in [AGH02]. In the latter work the reaction terms were written in a very special form involving the associated chemical potentials. The observation of this work is that these reaction terms can be written as 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 more general form than in [AGH02].

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 this 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 made to obtain evolutionary systems having a formal gradient structure. We hope 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, GIG09]) but also the gradient structure.

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

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

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 with the dual form obtained via the dual dissipation potential $\Psi^*(z, \cdot) : Z^* \rightarrow [0, \infty]$ obtained from $\Psi(z, \cdot) : Z \rightarrow [0, \infty]$ via Legendre transform:

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

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

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

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

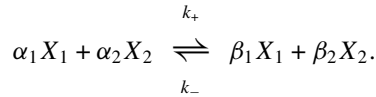
$$\dot{n} = \operatorname{div}(M(n)\nabla n) + R(n) \quad (1.3)$$

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, GIH97, 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 the 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. In the long run, the results of this work have the potential to improve or 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 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 were 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 coefficients 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



The associated reaction–diffusion systems for the densities $\mathbf{n} = (n_1, n_2)$ read

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

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

$$\mathcal{F}(\mathbf{n}) = \int_{\Omega} n_1(\log n_1 - 1) + n_2(\log n_2 - 1) \, dx,$$

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

$$\Psi^*(\mathbf{n}; \mu_1, \mu_2)$$

$$= \frac{1}{2} \int_{\Omega} n_1 d_1 |\nabla \mu_1|^2 + n_2 d_2 |\nabla \mu_2|^2 + k_+ \ell(n_1^{\alpha_1} n_2^{\alpha_2}, n_1^{\beta_1} n_2^{\beta_2}) \left(\begin{pmatrix} \alpha_1 - \beta_1 \\ \alpha_2 - \beta_2 \end{pmatrix} \cdot \begin{pmatrix} \mu_1 \\ \mu_2 \end{pmatrix} \right)^2 \, dx$$

with ℓ defined in (3.2). Using the *strong reversibility conditions* $k_+ = k_-$ it is easy to check that the dual gradient system $\dot{\mathbf{n}} = \mathbf{D}_{\mu} \Psi^*(\mathbf{n}; -\mathbf{D}\mathcal{F}(\mathbf{n}))$ gives exactly (1.4). Under the usual *reversibility condition* $k_{\pm} > 0$ the gradient structure is constructed in section 3.2.

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 3.6 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 potential, 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. 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 modelling in the form of generalized gradient flows. While gradient flows can be defined on general manifolds, we restrict ourselves to a linear state space Z . Nevertheless we use the notation $TZ = Z \times Z$ for the tangent bundle and $T^*Z = Z \times Z^*$ for the cotangent bundle, where Z^* is the dual space. Moreover, we write $T_zZ = \{z\} \times Z$ and $T_z^*Z = \{z\} \times Z^*$ for the (co-) tangent space at a point $z \in Z$. A function $\Psi : TZ \rightarrow [0, \infty]$ is called dissipation potential, if for each z the potential $\Psi(z, \cdot) : Z \rightarrow [0, \infty]$ satisfies $\Psi(z, 0) = 0$, lower semicontinuous, and convex. By $\partial_z \Psi$ we denote the (possibly multi-valued) convex subdifferential with respect to the second argument, namely

$$\partial_z \Psi(z, \dot{z}) = \{\zeta \in T_z^*Z \mid \Psi(z, v) \geq \Psi(z, \dot{z}) + \langle \zeta, v - \dot{z} \rangle \text{ for all } v \in T_zZ\}.$$

For a given energy functional $\Phi : Z \rightarrow \mathbb{R}$ we denote by $D\Phi(z) \in T_z^*Z$ the Fréchet differential. Then, the generalized gradient flow for the triple (Z, Φ, Ψ) is given in the form

$$0 \in \partial_z \Psi(z, \dot{z}) + D\Phi(z) \quad \text{in } T_zZ. \quad (2.1)$$

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

$$G(z)\dot{z} = -D\Phi(z) \quad \text{in } T_zZ. \quad (2.2)$$

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

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

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

$$\Phi(z(0)) - \Phi(z(t)) = \int_0^t \langle \partial_z \Psi(z, \dot{z}), \dot{z} \rangle dt \quad (2.4a)$$

$$= \int_0^t \Psi(z, \dot{z}) + \Psi^*(z, -D\Phi(z)) dt \quad (2.4b)$$

$$= \int_0^t \langle -D\Phi(z), \partial_\zeta \Psi^*(z, -D\Phi(z)) \rangle dt \quad (2.4c)$$

using the classical Legendre equivalence

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

Since the right-hand sides in (2.4a)–(2.4c) 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 already specifies the dynamics completely.

Remark 2.1 (Transformation rule). Often it is desirable to transform a gradient system for z via a transformation $z = \phi(\mathbf{p})$, where $\phi : \mathbf{P} \rightarrow \mathbf{Z}$ is a local diffeomorphism. Given (\mathbf{Z}, Φ, Ψ) we define the gradient system $(\mathbf{P}, \tilde{\Phi}, \tilde{\Psi})$ via

$$\tilde{\Phi}(\mathbf{p}) = \Phi(\phi(\mathbf{p})) \quad \text{and} \quad \tilde{\Psi}(\mathbf{p}, \dot{\mathbf{p}}) = \Psi(\phi(\mathbf{p}), D\phi(\mathbf{p})\dot{\mathbf{p}}).$$

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

$$\tilde{G}(\mathbf{p}) = D\phi(\mathbf{p})^* G(\phi(\mathbf{p})) D\phi(\mathbf{p}) \quad \text{and} \quad \tilde{\Psi}^*(\mathbf{p}, \boldsymbol{\mu}) = \Psi^*(\phi(\mathbf{p}), D\phi(\mathbf{p})^{-*} \boldsymbol{\mu}).$$

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 the case (i) we usually write the gradient system $(\mathbf{Z}, \mathcal{F}, \Psi)$ in the dual form $\dot{\mathbf{n}} = D_{\boldsymbol{\mu}} \Psi^*(\mathbf{n}, -D\mathcal{F}(\mathbf{n}))$, where \mathbf{n} is the vector of densities of the species and the vector $\boldsymbol{\mu} = D\mathcal{F}(\mathbf{n})$ of chemical potentials denotes the corresponding thermodynamic force dual to \mathbf{n} . The functional \mathcal{F} is decreasing and $2\Psi(\mathbf{n}; \dot{\mathbf{n}}) = 2\Psi^*(\mathbf{n}; -D\mathcal{F}(\mathbf{n}))$ gives the energy-dissipation rate.

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

$$(\dot{\mathbf{n}}, \dot{u}) = D_{\boldsymbol{\eta}, \tau} \Psi^*(\mathbf{n}, u; +D\mathcal{S}(\mathbf{n}, u)), \quad (2.5)$$

where the ‘+’ appears because $-S$ is a Liapunov function. The quantity $2\Psi(\mathbf{n}, u; \dot{\mathbf{n}}, \dot{u}) = 2\Psi^*(\mathbf{n}, u; D\mathcal{S}(\mathbf{n}, u))$ is called the entropy-production rate.

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

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

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

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

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 $\mathcal{C}_1, \dots, \mathcal{C}_m$, one can use the *principle of maximal entropy*, which means to maximize the (concave) entropy \mathcal{S} under the constraints $\mathcal{E}(z) = E_0$ and $\mathcal{C}_j(z) = C_j$. Under suitable assumptions one obtains an extremum z_{eq} and Lagrange multipliers $\lambda_0, \dots, \lambda_m \in \mathbb{R}$ such that

$$0 = D\mathcal{S}(z_{\text{eq}}) + \lambda_0 D\mathcal{E}(z_{\text{eq}}) + \lambda_1 D\mathcal{C}_1(z_{\text{eq}}) + \dots + \lambda_m D\mathcal{C}_m(z_{\text{eq}}).$$

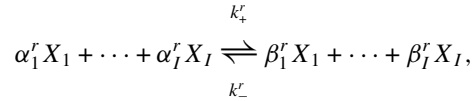
Having an invariance (2.6) but now also including \mathcal{C}_j it is easy to see that z_{eq} is actually a steady state of the gradient system (2.5).

3. Reaction–diffusion systems

The aim of this section is to show that reaction–diffusion systems of the type (1.2) may have a gradient structure, if 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. Strongly reversible reactions

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



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

$$\dot{\mathbf{n}} = \mathbf{R}(\mathbf{n}) := \sum_{r=1}^R -(k_+^r(\mathbf{n})\mathbf{n}^{\alpha^r} - k_-^r(\mathbf{n})\mathbf{n}^{\beta^r})(\alpha^r - \beta^r), \quad (3.1)$$

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

The r th reaction is called *strongly reversible*, if $k_+^r = k_-^r$. We call the reaction system strongly reversible, if all reactions are strongly reversible, i.e. $k_\pm^r = k^r$. The main observation is that under this condition we can write (3.1) as a gradient systems as follows. Afterwards, we show that the construction can be generalized to general reversible reaction systems, if they satisfy the condition of detailed balance. However, to keep the notations in the rest of the paper simple, we will restrict ourselves to the case of strongly reversible reaction systems. The generalization is straightforward and can be found, e.g., in [GIM11].

We define the free energy as $F(\mathbf{n}) = \sum_{i=1}^I n_i (\log n_i - 1)$, which gives the chemical potentials $\mathbf{D}F(\mathbf{n}) = \boldsymbol{\mu} = (\mu_1, \dots, \mu_m) \in \mathbb{R}^I$ with $\mu_i = \log n_i$. We define the dual dissipation potential

$$\psi^*(\mathbf{n}, \boldsymbol{\mu}) = \sum_{r=1}^R \frac{k^r(\mathbf{n})}{2} \ell(\mathbf{n}^{\alpha^r}, \mathbf{n}^{\beta^r}) \left((\alpha^r - \beta^r) \cdot \boldsymbol{\mu} \right)^2$$

$$\text{with } \ell(x, y) = \begin{cases} \frac{x - y}{\log x - \log y} & \text{for } x \neq y, \\ y & \text{for } x = y. \end{cases} \quad (3.2)$$

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

The stoichiometric subspace \mathbb{S} and its orthogonal complement \mathbb{S}^\perp are defined via $\mathbb{S} := \text{span}\{\alpha^r - \beta^r \mid r = 1, \dots, R\} \subset \mathbb{R}^I$, $\mathbb{S}^\perp := \{\boldsymbol{\xi} \in \mathbb{R}^I \mid \boldsymbol{\xi} \cdot \boldsymbol{\mu} = 0 \text{ for all } \boldsymbol{\mu} \in \mathbb{S}\}$. (3.3) Then for each $\boldsymbol{\xi} \in \mathbb{S}^\perp$ the function $C_\xi(\mathbf{n}) = \boldsymbol{\xi} \cdot \mathbf{n}$ defines a first integral, which is easily checked using $\psi^*(\mathbf{n}, \boldsymbol{\mu} + \boldsymbol{\xi}) = \psi^*(\mathbf{n}, \boldsymbol{\mu})$. These conservation laws often go under the name *conservation of atomic species*, see [ErT89].

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

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

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 $\mathbf{H}(\mathbf{n})$ is strictly positive definite on \mathbb{S} . Thus, the Legendre transform $\psi(\mathbf{n}, \cdot) : \mathbb{R}^I \rightarrow [0, \infty]$ of $\psi^*(\mathbf{n}, \cdot) : \mathbb{R}^I \rightarrow [0, \infty]$ can be easily calculated in the form

$$\psi(\mathbf{n}, \mathbf{v}) = \begin{cases} \left(\frac{1}{2} \mathbf{H}(\mathbf{n})^+ \mathbf{v} \right) \cdot \mathbf{v} & \text{for } \mathbf{v} \in \mathbb{S}, \\ \infty & \text{for } \mathbf{v} \notin \mathbb{S}, \end{cases} \quad (3.4)$$

where H^+ denotes the pseudo-inverse (Moore–Penrose inverse) of H . Thus, the gradient systems read

$$0 = D_{\dot{n}}\psi(\mathbf{n}, \dot{\mathbf{n}}) + DF(\mathbf{n}).$$

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

Summing up the above derivations we have rewritten the reaction system in thermodynamic form

$$\dot{\mathbf{n}} = \mathbf{R}(\mathbf{n}) = -\mathbf{H}(\mathbf{n})\boldsymbol{\mu} \quad \text{with } \boldsymbol{\mu} = DF(\mathbf{n}). \tag{3.5}$$

Hence, $\mathbf{H}(\mathbf{n}) \in \mathbb{R}_{\text{spsd}}^{I \times I}$ can be seen as the symmetric Onsager matrix containing the kinetic coefficients, see, e.g., [DeM84, chapter X, section 4].

3.2. Reversible reactions with detailed balance

Here we show that the condition of strong reversibility is not really needed. Instead it is sufficient that the reaction system is reversible and satisfies the condition of *detailed balance* (which is also called the condition of *microscopic reversibility*). We refer to [DeM84] for a general discussion of these concepts.

The condition of detailed balance for the reaction system means for the reaction rates k_+^r and k_-^r that there exists a steady state $\mathbf{n}_\circ = (n_1^\circ, \dots, n_I^\circ) \in]0, \infty[^I$ such that

$$k_+^r(\mathbf{n})n_\circ^{\alpha^r} = k_-^r(\mathbf{n})n_\circ^{\beta^r} \quad \text{for all } \mathbf{n} \in]0, \infty[^I \quad \text{and } r \in \{1, \dots, R\}, \tag{3.6}$$

see [ErT89, p 45]. Obviously, this implies the steady-state condition $\mathbf{R}(\mathbf{n}_\circ) = 0$ in such a way that each term in the sum in (3.1) is 0. This explains the name ‘detailed balance’ as each reaction is in equilibrium.

If the reaction rates k_\pm^r are constant, then condition (3.6) can be recast as a linear system for the unknowns $\log n_i^\circ, i = 1, \dots, I$, which are then called the Wegscheider conditions, see, e.g., [ScS89, GIM11]. Hence, if the number R of reactions is smaller than the number I of species this condition can usually be satisfied easily.

Using the steady state \mathbf{n}_\circ we define the energy functional F_\circ and the dual dissipation potential ψ_\circ^* via

$$F_\circ(\mathbf{n}) = \sum_{i=1}^I n_i \left(\log \left(\frac{n_i}{n_i^\circ} \right) - 1 \right)$$

and

$$\psi_\circ^*(\mathbf{n}, \boldsymbol{\mu}) = \sum_{r=1}^R \frac{k_\circ^r(\mathbf{n})}{2} \ell \left(\frac{\mathbf{n}^{\alpha^r}}{n_\circ^{\alpha^r}}, \frac{\mathbf{n}^{\beta^r}}{n_\circ^{\beta^r}} \right) (\boldsymbol{\mu} \cdot (\boldsymbol{\alpha}^r - \boldsymbol{\beta}^r))^2.$$

It is now easy to see that the reaction system (3.1) is generated by the gradient system $(\mathbb{R}^I, F_\circ, \psi_\circ)$, namely $\dot{\mathbf{n}} = \mathbf{R}(\mathbf{n}) = D_\mu \Psi_\circ^*(\mathbf{n}, -DF_\circ(\mathbf{n}))$.

Remark 3.1 (Relative entropy). The above construction of F_\circ can be understood in the sense of ‘relative entropy’. In many cases the (entropic part of the isothermal) free energy F can be written in the form $F(\mathbf{n}) = \sum_{i=1}^I f_i(n_i)$. For a given state $\mathbf{n}_\circ = (n_1^\circ, \dots, n_I^\circ)$ the construction is $F_\circ(\mathbf{n}) = \sum_{i=1}^I n_i^\circ f_i(n_i/n_i^\circ)$. If $f_i(v) = v(\log v - 1)$, then $F_\circ(\mathbf{n}) = F(\mathbf{n}) - \mathbf{a} \cdot \mathbf{n}$ with $\mathbf{a} = (\log n_i^\circ)_{i=1, \dots, I}$ and $DF_\circ(\mathbf{n}) = (\log n_i - a_i)_{i=1, \dots, I}$.

3.3. Diffusion systems

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

$$\dot{\mathbf{n}} = \operatorname{div}(\tilde{\mathbb{M}}(\mathbf{n})\nabla\mathbf{n}) \quad \text{for } x \in \Omega, \quad \tilde{\mathbb{M}}(\mathbf{n})\nabla\mathbf{n} \cdot \nu = 0 \quad \text{on } \partial\Omega. \quad (3.7)$$

Here $\nabla\mathbf{n} \in \mathbb{R}^{I \times d}$ and $\tilde{\mathbb{M}}(\mathbf{n}) \in \operatorname{Lin}(\mathbb{R}^{I \times d}; \mathbb{R}^{I \times d})$.

The main question we want to answer in this section is the following: for which diffusion tensors $\tilde{\mathbb{M}}$ the above diffusion system has a gradient structure with respect to the same free energy as above, namely $\mathcal{F}(\mathbf{n}) = \int_{\Omega} F(\mathbf{n}(x)) \, dx$ where $F(\mathbf{n}) = \sum_{i=1}^I n_i (\log n_i - 1)$.

To answer this question we start from a general dual dissipation functional

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

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

$$\dot{\mathbf{n}} = D_{\boldsymbol{\mu}}\Psi_{\text{diff}}^*(\mathbf{n}, -D\mathcal{F}(\mathbf{n})) = \operatorname{div}(\mathbb{M}(\mathbf{n})D_n\nabla\mathbf{n}) \quad \text{with} \quad D_n := \operatorname{diag}\left(\frac{1}{n_1}, \dots, \frac{1}{n_I}\right).$$

Thus, we reveal that if (3.7) has a gradient structure with energy \mathcal{F} then $\tilde{\mathbb{M}}(\mathbf{n})$ necessarily has the form

$$\tilde{\mathbb{M}}(\mathbf{n}) = \mathbb{M}(\mathbf{n})D_n \quad \text{with} \quad \mathbb{M}(\mathbf{n}) = \mathbb{M}(\mathbf{n})^* \geq 0, \quad \text{where} \quad D_n = D^2\mathcal{F}(\mathbf{n}). \quad (3.8)$$

The construction of a suitable \mathbb{M} for a given $\tilde{\mathbb{M}}$ is simple, if there is no cross-diffusion, i.e. $\tilde{\mathbb{M}}$ satisfies

$$\operatorname{div}(\tilde{\mathbb{M}}(\mathbf{n})\nabla\mathbf{n}) = \left(\operatorname{div}(\tilde{M}_i(\mathbf{n})\nabla n_i)\right)_{i=1, \dots, I} \quad \text{with} \quad \tilde{M}_i(\mathbf{n}) \in \mathbb{R}_{\text{spsd}}^{d \times d}.$$

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

$$\dot{\mathbf{n}} = \operatorname{diag}(\tilde{M}_1, \dots, \tilde{M}_I)\Delta\mathbf{n}.$$

For systems with cross-diffusion the situation is more complicated, since unsymmetries and nontrivial dependences on \mathbf{n} will appear. We highlight this difficulty by considering the case of two species in a one-dimensional medium $\Omega \subset \mathbb{R}$. We then write $\nabla\mathbf{n} = (n'_1, n'_2)$ with $' = \partial/\partial x$. Now, condition (3.8) shows that the diffusion system (3.7) reduces to

$$\begin{pmatrix} \dot{n}_1 \\ \dot{n}_2 \end{pmatrix} = \left(\begin{pmatrix} m_1(\mathbf{n})/n_1 & m_{\text{cross}}(\mathbf{n})/n_2 \\ m_{\text{cross}}(\mathbf{n})/n_1 & m_2(\mathbf{n})/n_2 \end{pmatrix} \begin{pmatrix} n'_1 \\ n'_2 \end{pmatrix} \right)',$$

$$\text{where } m_1(\mathbf{n})m_2(\mathbf{n}) \geq m_{\text{cross}}(\mathbf{n})^2.$$

Clearly the diffusion tensor is symmetric only if $m_{\text{cross}}(\mathbf{n}) = 0$ or $n_1 = n_2$.

Note that there is a second source of cross-diffusion, which is excluded here because \mathcal{F} is a sum of functionals depending on one n_i only. If $D_{n_i}\mathcal{F}(\mathbf{n})$ depends on n_j also, then coupling occurs, even if \mathbb{M} is diagonal. Such couplings occur in the temperature-dependent cases and in the semiconductor equations discussed below.

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

$$\Psi_{\text{diff}}(\mathbf{n}, \mathbf{v}) = \int_{\Omega} \frac{1}{2} \mathbf{v} \cdot \mathcal{M}_n^{-1} \mathbf{v} \, dx = \int_{\Omega} \frac{1}{2} \mathbf{v} \cdot \boldsymbol{\mu}_n^{\mathbf{v}} \, dx = \int_{\Omega} \frac{1}{2} \nabla\boldsymbol{\mu}_n^{\mathbf{v}} \cdot \mathbb{M}(\mathbf{n})\nabla\boldsymbol{\mu}_n^{\mathbf{v}} \, dx, \quad (3.9)$$

where μ_n^v is the unique solution in X_{00} of

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

Thus, we have found the formal gradient system

$$0 = D_{\dot{n}} \Psi_{\text{diff}}(n, \dot{n}) + D\mathcal{F}(n) \iff \dot{n} = D\Psi_{\text{diff}}^*(n, -D\mathcal{F}(n)).$$

3.4. 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 $X = L^1(\Omega; \mathbb{R}^I)$ and the functionals

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

with ψ^* for section 3.1.

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

$$X_0 := \left\{ n \in X \mid \int_{\Omega} n(x) \, dx \in \mathbb{S} \right\},$$

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

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

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

$$\Psi(n, v) = \int_{\Omega} \frac{1}{2} v \cdot \mathcal{A}_n^{-1} v \, dx = \int_{\Omega} \frac{1}{2} v \cdot \tilde{\mu}_n^v \, dx = \Psi^*(n, \tilde{\mu}_n^v),$$

where $\tilde{\mu}_n^v$ is the unique solution in X_0 of

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

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

$$\Psi(n, v) = \inf \{ \Psi_{\text{diff}}(n, v_1) + \Psi_{\text{react}}(n, v_2) \mid v_1 + v_2 = v \}$$

where Ψ_{diff} is defined in (3.9) while Ψ_{react} is obtained from ψ in (3.4) via integration over Ω . Altogether, we have established the gradient form

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

3.5. A strongly reversible reaction–diffusion system

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 strongly reversible reaction $pX_1 \rightleftharpoons qX_2$. The reaction–diffusion system

$$\dot{n}_1 = M_1 \Delta n_1 - kp(n_1^p - n_2^q), \quad \dot{n}_2 = M_2 \Delta n_2 + kq(n_1^p - n_2^q) \quad \text{in } \Omega, \quad (3.10)$$

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 [PSV10].

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

$$\Psi^*(n_1, n_2; \mu_1, \mu_2) = \frac{1}{2} \int_{\Omega} n_1 M_1 |\nabla \mu_1|^2 + n_2 M_2 |\nabla \mu_2|^2 + k\ell(n_1^p, n_2^q)(p\mu_1 - q\mu_2)^2 \, dx,$$

where ℓ is given in (3.2). Obviously, $\mathbb{S}^{\perp} = \text{span} \left(\begin{smallmatrix} q \\ p \end{smallmatrix} \right)$ and $\mathcal{C}(n_1, n_2) = \int_{\Omega} qn_1 + pn_2 \, dx$ is a conserved quantity.

For the given initial value $(n_1(0), n_2(0)) \in H^1(\Omega; \mathbb{R}^2)$ the unique solution of (3.10) will converge to the unique steady state which is the minimizer of $\mathbf{n} \mapsto \mathcal{F}(\mathbf{n})$ subjected to the constraint $\mathcal{C}(\mathbf{n}) = \mathcal{C}(n_1(0), n_2(0))$, which is a spatially constant state.

3.6. Reaction–diffusion systems with temperature coupling

As the 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 the role of the driving functional. To model temperature effects we have several choices for 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 $u : \Omega \rightarrow \mathbb{R}$, which leads to the functionals

$$\mathcal{E}(\mathbf{n}, u) = \int_{\Omega} u \, dx \quad \text{and} \quad \mathcal{S}(\mathbf{n}, u) = \int_{\Omega} S(\mathbf{n}(x), u(x)) \, dx$$

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

$$\boldsymbol{\eta} = D_{\mathbf{n}} \mathcal{S}(\mathbf{n}, u) = \partial_{\mathbf{n}} \mathcal{S}(\mathbf{n}, u), \quad \tau = D_u \mathcal{S}(\mathbf{n}, u) = \partial_u \mathcal{S}(\mathbf{n}, u),$$

where, by standard thermodynamic modelling, $\theta = 1/\tau > 0$ is the absolute temperature.

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

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

where $M(\mathbf{n}, u)$ is a symmetric and positive semi-definite tensor in $\text{Lin}(\mathbb{R}^{(I+1) \times d}; \mathbb{R}^{(I+1) \times d})$, which contains the (cross-) diffusion coefficients for the density vector \mathbf{n} as well as the symmetric heat conduction tensor for $(M_{I+1, \alpha, I+1, \beta})_{\alpha, \beta=1, \dots, d}$. The reactive dual dissipation potential ψ^* is given as in section 3.1, but now the reaction rates may depend on the temperature via the internal energy, i.e.

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

Here the coefficients \widehat{k}^r are different from k^r in (3.2), since η has the physical dimension of μ divided by temperature (e.g. we may take $k^r = \theta^2 k^r$). In particular, Ψ^* is now the dual entropy-production potential.

Using $D\mathcal{E}(\mathbf{n}, u) = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$, we easily find the invariance

$$\Psi^*(\mathbf{n}, u; \begin{pmatrix} \eta \\ \tau \end{pmatrix}) + \lambda_1 D\mathcal{E} + \lambda_2 DC\xi = \Psi^*(\mathbf{n}, u, \eta, \tau) \quad \text{for all } \lambda_1, \lambda_2 \in \mathbb{R}, \xi \in \mathbb{S}^\perp. \quad (3.11)$$

The dual gradient system $\begin{pmatrix} \dot{\mathbf{n}} \\ \dot{u} \end{pmatrix} = D_{(\eta, \tau)} \Psi^*(\mathbf{n}, u; DS(\mathbf{n}, u))$ takes the form

$$\begin{aligned} \dot{\mathbf{n}} &= -\operatorname{div} j_{\mathbf{n}} + \widehat{H}(\mathbf{n}, u) \partial_{\mathbf{n}} S(\mathbf{n}, u), & \begin{pmatrix} j_{\mathbf{n}} \\ j_u \end{pmatrix} &= M(\mathbf{n}, u) \begin{pmatrix} \nabla \partial_{\mathbf{n}} S(\mathbf{n}, u) \\ \nabla \partial_u S(\mathbf{n}, u) \end{pmatrix}. \end{aligned} \quad (3.12)$$

Using the no-flux boundary conditions it is easy to see that the total energy \mathcal{E} and all C_ξ 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 $\overline{F}(\mathbf{n}, \theta)$ we may define the relations

$$u = \overline{U}(\mathbf{n}, \theta) := \overline{F}(\mathbf{n}, \theta) - \theta \partial_\theta \overline{F}(\mathbf{n}, \theta), \quad s = \overline{S}(\mathbf{n}, \theta) := -\partial_\theta \overline{F}(\mathbf{n}, \theta). \quad (3.13)$$

We arrive at the functionals

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

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

$$\overline{\Psi}^*(\mathbf{n}, \theta; \mu_{\mathbf{n}}, \mu_\theta) = \Psi^* \left(\mathbf{n}, \overline{U}(\mathbf{n}, \theta); \mu_{\mathbf{n}} - \frac{\mu_\theta}{\partial_\theta \overline{U}(\mathbf{n}, \theta)} \partial_{\mathbf{n}} \overline{U}(\mathbf{n}, \theta), \frac{\mu_\theta}{\partial_\theta \overline{U}(\mathbf{n}, \theta)} \right).$$

Thus, (3.12) is equivalent to a dual gradient system for (\mathbf{n}, θ) in the form

$$\begin{pmatrix} \dot{\mathbf{n}} \\ \dot{\theta} \end{pmatrix} = D\overline{\Psi}^*(\mathbf{n}, \theta, D_{\mathbf{n}} \overline{S}(\mathbf{n}, \theta), D_\theta \overline{S}(\mathbf{n}, \theta)).$$

Again we have conservation of energy via $\Psi^*(\mathbf{n}, \theta; (\eta, \mu_\theta) + \lambda D_{\mathbf{n}, \theta} \overline{\mathcal{E}}) = \Psi^*(\mathbf{n}, \theta; \eta, \mu_\theta)$. Moreover, using the definition of \overline{U} and \overline{S} via \overline{F} in (3.13) we obtain

$$\begin{aligned} \partial_{\mathbf{n}} \overline{S} - \frac{\partial_\theta \overline{S}}{\partial_\theta \overline{U}} \partial_{\mathbf{n}} \overline{U} &= -\frac{1}{\theta} \partial_{\mathbf{n}} \overline{F}, & \frac{\partial_\theta \overline{S}}{\partial_\theta \overline{U}} &= \frac{1}{\theta}, \\ \overline{\Psi}^*(\mathbf{n}, \theta; D_{\mathbf{n}} \overline{S}(\mathbf{n}, \theta), D_\theta \overline{S}(\mathbf{n}, \theta)) &= \Psi^* \left(\mathbf{n}, \overline{U}(\mathbf{n}, \theta); \frac{1}{\theta} \partial_{\mathbf{n}} \overline{F}(\mathbf{n}, \theta), \frac{1}{\theta} \right). \end{aligned}$$

This leads to a coupled system for (\mathbf{n}, θ) in the form

$$\begin{aligned} \dot{\mathbf{n}} &= -\operatorname{div} j_{\mathbf{n}} - \frac{1}{\theta} \overline{H}(\mathbf{n}, \theta) \partial_{\mathbf{n}} \overline{F}(\mathbf{n}, \theta), \\ \dot{\theta} &= \frac{1}{\partial_\theta \overline{U}} \left(-\operatorname{div} j_\theta + \partial_{\mathbf{n}} \overline{U} \cdot \operatorname{div} j_{\mathbf{n}} + \frac{1}{\theta} \partial_{\mathbf{n}} \overline{U} \cdot \overline{H}(\mathbf{n}, \theta) \partial_{\mathbf{n}} \overline{F}(\mathbf{n}, \theta) \right), \end{aligned}$$

where

$$\overline{H}(\mathbf{n}, \theta) = \widehat{H}(\mathbf{n}, \overline{U}(\mathbf{n}, \theta)) \quad \text{and} \quad \begin{pmatrix} j_{\mathbf{n}} \\ j_\theta \end{pmatrix} = M(\mathbf{n}, \overline{U}(\mathbf{n}, \theta)) \nabla \begin{pmatrix} -\frac{1}{\theta} \partial_{\mathbf{n}} \overline{F} \\ \frac{1}{\theta} \end{pmatrix}. \quad (3.14)$$

In this system we clearly see the influence of reactions on the temperature and vice versa. Moreover, the above derivation shows that (3.14) is a gradient system for the driving functional $-\overline{S}$ 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

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

For the internal energy and the entropy we obtain

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

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

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

We may simplify further by assuming $M_{\theta\theta}(\mathbf{n}, \theta) = \theta^2 m I$, 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, GIG09].

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 section 3.2. 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 $\mathbf{n} = (n, p) : \Omega \rightarrow]0, \infty[^2$ generates an electrostatic potential ϕ_n as the unique solution of the linear potential equation

$$-\Delta \phi = \delta - n + p \text{ in } \Omega, \quad \phi = \phi_{\text{Dir}} \text{ on } \partial\Omega, \quad (4.1a)$$

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

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

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

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

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

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:

$$\mathcal{E}(\mathbf{n}) = \int_{\Omega} \frac{1}{2} |\nabla \phi_n|^2 + F(n, p) \, dx \quad \text{and} \quad \mathcal{Q}(\mathbf{n}) = \int_{\Omega} \delta - n + p \, dx,$$

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

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

The components of $\boldsymbol{\mu}$ are called electrochemical potentials as they are a sum of the chemical potential DF and the potential ϕ_n multiplied with the corresponding charge. It is astonishing here that $\boldsymbol{\mu} = D\mathcal{E}(\mathbf{n})$ contains ϕ_n without any derivative. To see this one has to use that ϕ_n solves (4.1a) and depends linearly on \mathbf{n} , see [AGH02, lemma 6.1]. The dual dissipation potential is chosen as

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

where ℓ is defined in (3.2). Thus, we again have two Wasserstein terms for the mobilities plus a reaction term.

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

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

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

4.2. Energy-drift-diffusion equations with recombination

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

According to [AGH02, theorem 6.2 and remark 7.3], the balance equations take the form

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

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

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

(In the case $\Gamma_{\text{Dir}} = \emptyset$ the electric potential ϕ is only defined up to an additive constant. Such a constant does not affect the equations because \mathcal{E} depends on $\nabla \phi$ only and its derivative $D_n \mathcal{E} = \phi_n \mathbf{q}$ enters the model only via $\nabla \boldsymbol{\mu}$, see below.) Here δ is a doping profile, ϕ is the

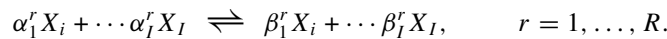
electrostatic potential, and $\varepsilon > 0$ is the electric permittivity (tensor). For the fluxes one now takes the ansatz

$$\begin{pmatrix} j_n \\ j_u \end{pmatrix} = M(\mathbf{n}, u) \nabla \begin{pmatrix} \tilde{\eta} \\ \tau \end{pmatrix}, \quad (4.3)$$

where the mobility tensor M is assumed to be symmetric and positive semi-definite. (In the case of immobile species, some entries of M will be 0 to forbid motion of the species by diffusion or drift.) As before, $(\tilde{\eta}, \tau)$ will be suitable thermodynamic driving forces associated with (\mathbf{n}, u) obtained from the entropy functional. As before, the recombination terms \mathbf{R} will be given in the form

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

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



(As explained in section 3.2 it would be sufficient to have reactions satisfying the detailed balance condition and renormalizing the densities suitably.) We define the dual reaction potential

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

Note that we have subsumed the previous product $k^r(\mathbf{n}, u)\ell(\mathbf{n}^{\alpha^r}, \mathbf{n}^{\beta^r})$ into one constant $K_r(\mathbf{n}, u)$. 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 \mathbf{R} , see section 4.3.

The important point in electrochemical reactions is that each reaction preserves the total amount of electric charge. Using the stoichiometric subspace $\mathbb{S} \subset \mathbb{R}^l$ introduced in (3.3) and its orthogonal complement \mathbb{S}^\perp , this simply means $\mathbf{q} \in \mathbb{S}^\perp$. Hence, ψ^* satisfies the invariance $\psi^*(\mathbf{n}, u; \boldsymbol{\eta} + \lambda \mathbf{q}) = \psi^*(\mathbf{n}, u; \boldsymbol{\eta})$ for all $\lambda \in \mathbb{R}$, which implies $\mathbf{R}(\mathbf{n}, u) \cdot \mathbf{q} \equiv 0$.

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

$$\mathcal{Q}(\mathbf{n}, u) = \int_{\Omega} \delta + \mathbf{q} \cdot \mathbf{n} \, dx, \quad \mathcal{E}(\mathbf{n}, u) = \int_{\Omega} \frac{1}{2} \nabla \phi_n \cdot \varepsilon \nabla \phi_n + u \, dx,$$

$$\mathcal{S}(\mathbf{n}, u) = \int_{\Omega} S(\mathbf{n}, u) \, dx,$$

respectively, where ϕ_n is the unique solution of the Poisson equation (4.2c). The entropy density $S(\mathbf{n}, u)$ encodes the material properties in dependence on the temperature, but now expressed in terms of the internal energy. In [AGH02, proposition 3.2] it is shown that it is physically reasonable (for certain semiconductor materials) to assume that $S :]0, \infty[\times \mathbb{R} \rightarrow \mathbb{R}$ is strictly concave. Recall that the physical entropy \mathcal{S} wants to increase, so that $-\mathcal{S}$ is a Liapunov function, such that convexity of $-\mathcal{S}$ is a good property.

For the differentials we obtain the expressions

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

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

We first check that the semiconductor system (4.2a)–(4.2c) is thermodynamically consistent in the sense of [AGH02], namely 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 $\tilde{\eta}$ in the flux relation (4.3). We follow [AGH02] and let

$$\tilde{\eta} = D_n S(\mathbf{n}, u) - \frac{1}{\theta} D_n \mathcal{E}(\mathbf{n}, u) = \partial_n S(\mathbf{n}, u) - \partial_u S(\mathbf{n}, u) \phi_n \mathbf{q}.$$

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

$$\begin{aligned} \frac{d}{dt} \mathcal{Q}(\mathbf{n}, u) &= \langle D\mathcal{Q}(\mathbf{n}, u), (\dot{\mathbf{n}}, \dot{u}) \rangle \\ &= \int_{\Omega} \mathbf{q} \cdot (\mathbf{R} - \operatorname{div} \mathbf{j}_n) \, dx = - \int_{\Omega} \operatorname{div} \mathbf{q} \cdot \mathbf{j}_n \, dx = 0; \\ \frac{d}{dt} \mathcal{E}(\mathbf{n}, u) &= \langle D\mathcal{E}(\mathbf{n}, u), (\dot{\mathbf{n}}, \dot{u}) \rangle \\ &= \int_{\Omega} \phi_n \mathbf{q} \cdot (\mathbf{R} - \operatorname{div} \mathbf{j}_n) - \operatorname{div} j_u + \phi_n \mathbf{q} \cdot \operatorname{div} \mathbf{j}_n \, dx = - \int_{\Omega} \operatorname{div} j_u \, dx = 0; \\ \frac{d}{dt} S(\mathbf{n}, u) &= \langle DS(\mathbf{n}, u), (\dot{\mathbf{n}}, \dot{u}) \rangle = \int_{\Omega} \partial_n S(\mathbf{n}, u) \cdot \dot{\mathbf{n}} + \partial_u S(\mathbf{n}, u) \dot{u} \, dx \\ &= \int_{\Omega} \left(\tilde{\eta} + \frac{\phi_n}{\theta} \mathbf{q} \right) \cdot (\mathbf{R} - \operatorname{div} \mathbf{j}_n) + \frac{1}{\theta} (- \operatorname{div} j_u + \phi_n \mathbf{q} \cdot \operatorname{div} \mathbf{j}_n) \, dx \\ &= \int_{\Omega} -\tilde{\eta} \cdot \operatorname{div} \mathbf{j}_n - \frac{\operatorname{div} j_u}{\theta} + \tilde{\eta} \cdot \mathbf{R} \, dx = \int_{\Omega} -\operatorname{div} j_s + \sigma_{\nabla} + \sigma_R \, dx \end{aligned}$$

with $j_s = \tilde{\eta} \cdot \mathbf{j}_n + \frac{1}{\theta} j_u$, $\sigma_{\nabla} = \nabla \left(\frac{\tilde{\eta}}{\tau} \right) \cdot M \nabla \left(\frac{\tilde{\eta}}{\tau} \right) \geq 0$, and $\sigma_R = \tilde{\eta} \cdot \mathbf{R} \geq 0$.

Here we used $\mathbf{q} \cdot \mathbf{R} \equiv 0$ several times as well as the no-flux boundary conditions $\mathbf{j}_n \cdot \nu = 0$ 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 σ_R of the reaction terms is nonnegative because of (4.4) and $\mathbf{q} \cdot \mathbf{R} \equiv 0$ giving

$$\sigma_R = \tilde{\eta} \cdot \mathbf{R}(\mathbf{n}, u) = \boldsymbol{\eta} \cdot \mathbf{H}(\mathbf{n}, u) \boldsymbol{\eta} \geq 0.$$

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 $\tilde{\eta}$ in the mobility term while we have to use the $\boldsymbol{\eta}$ in the reaction term:

$$\Psi^*(\mathbf{n}, u; \boldsymbol{\eta}, \tau) = \int_{\Omega} \frac{1}{2} \nabla \left(\frac{\boldsymbol{\eta} - \tau \phi_n \mathbf{q}}{\tau} \right) \cdot M(\mathbf{n}, u) \nabla \left(\frac{\boldsymbol{\eta} - \tau \phi_n \mathbf{q}}{\tau} \right) + \psi^*(\mathbf{n}, u, \boldsymbol{\eta}) \, dx. \tag{4.5}$$

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

$$\begin{pmatrix} j_n \\ j_u \end{pmatrix} = M(\mathbf{n}, u) \nabla \left(\frac{\tilde{\eta}}{\tau} \right) = M(\mathbf{n}, u) \begin{pmatrix} \nabla \left(\partial_n S(\mathbf{n}, u) - \frac{\phi_n}{\theta} \mathbf{q} \right) \\ \nabla(1/\theta) \end{pmatrix}.$$

Second, charge and energy conservation are obtained from the invariance

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

Third, it produces the source term $\phi_n \mathbf{q} \cdot \operatorname{div} \mathbf{j}_n$ in the energy balance.

The latter statement and the derivation of the differential equation generated by the dual gradient system $\frac{d}{dt} \begin{pmatrix} n \\ u \end{pmatrix} = D_{(\eta, \tau)} \Psi^*(n, u, DS(n, u))$ are obtained by noting the relation

$$\langle (\widehat{\eta}, \widehat{\tau}), D\Psi^*(n, u; DS(n, u)) \rangle = \int_{\Omega} \nabla \begin{pmatrix} \widehat{\eta} - \widehat{\tau} \frac{\phi_n}{\theta} \mathbf{q} \\ \widehat{\tau} \end{pmatrix} \cdot \begin{pmatrix} j_n \\ j_u \end{pmatrix} + \widehat{\eta} \cdot \mathbf{H}(n, u) \partial_n S(n, u) \, dx,$$

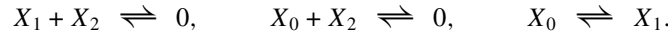
which holds for all $(\widehat{\eta}, \widehat{\tau})$. Comparing with $\langle (\widehat{\eta}, \widehat{\tau}), (\dot{n}, \dot{u}) \rangle$ we easily obtain the equations

$$\dot{n} = -\operatorname{div} j_n + \mathbf{H}(n, u) \partial_n S(n, u), \quad \dot{u} = -\operatorname{div} j_u + \phi_n \mathbf{q} \cdot \operatorname{div} j_n,$$

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 $\widetilde{k}^{ij}(n, u)(e^{q_j \eta_j - q_i \eta_i} - 1)\alpha$. Obviously, these terms can be rewritten in the linear form $K^{ij}(n, u)(q_j \eta_j - q_i \eta_i)$ where $K^{ij}(n, u) = k^{ij}(n, u)\ell(e^{m_{ij}(n, u)}, 1)$ with $m_{ij} = q_j \partial_{n_i} S - q_i \partial_{n_j} S$.

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



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

$$\widehat{\psi}^*(n, \theta; \eta) = \varrho_0(n, \theta) \Xi(\eta_1 + \eta_2) + \varrho_1(n, \theta) \Xi(\eta_0 + \eta_2) + \varrho_2(n, \theta) \Xi(\eta_1 - \eta_0),$$

where $\Xi(t) = e^t - 1 - t$. Hence $\widehat{\psi}^*(n, \theta; \cdot) : \mathbb{R}^3 \rightarrow [0, \infty[$ is smooth, strictly convex, and satisfies $\widehat{\psi}^*(n, \theta; 0) = 0$. 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).

4.3. Fermi–Dirac statistics

In semiconductor models it is often desirable to replace the Boltzmann statistics by the more accurate Fermi–Dirac statistics. In [AGH02, equation (1)] the following form for the free energy \bar{F} is suggested (k_B is Boltzmann’s constant):

$$\bar{F}(n, \theta) = c\theta(1 - \log \theta) - \sum_{i=1}^I q_i n_i E_i(\theta) + k_B \theta \sum_{i=1}^I n_i^\circ(\theta) f_i(n_i/n_i^\circ(\theta)), \tag{4.6}$$

where E_i denotes suitable energy levels and n_i° state densities (see section 3.2), which now depend on the temperature. See also remark 3.1 for the origins of relative entropies. Here the functions f_i give rise to the driving forces

$$\eta_i = \partial_{n_i} S(n, u) = -\frac{1}{\theta} \partial_{n_i} \bar{F}(n, \theta) = -k_B f_i'(n_i/n_i^\circ(\theta)) + \frac{q_i}{\theta} E_i(\theta).$$

In the Boltzmann case one assumes $f_i'(v) = \log v$ and obtains $f_i(v) = v(\log v - 1)$ and

$$n_i = n_i^\circ(\theta) \exp\left(\left(\frac{q_i}{\theta} E_i(\theta) - \eta_i\right) / k_B\right).$$

In the case of higher densities this exponential law may no longer be correct and needs to be replaced by the Fermi–Dirac statistics

$$n_i = n_i^\circ(\theta) \mathbb{F}_\gamma\left(\left(\frac{q_i}{\theta} E_i(\theta) - \eta_i\right) / k_B\right)$$

with

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

where the index satisfies $\gamma > -1$ and is usually taken to be $1/2$ for parabolic band edges. The Fermi integrals \mathbb{F}_γ satisfy $\mathbb{F}'_\gamma = \mathbb{F}_{\gamma-1}$ and $\mathbb{F}_\gamma(\mu) \approx e^\mu$ and $\mathbb{F}_\gamma(\mu) \approx \varrho_\gamma \mu^\gamma$ for $\mu \ll 0$ and $\mu \gg 0$, respectively. To construct the corresponding f_i in (4.6) we choose f'_i as inverse of $\mathbb{F}_{\gamma-1}$ and obtain $f_i(v) = v\mathbb{F}_{\gamma-1}^{-1}(v) - \mathbb{F}_\gamma(\mathbb{F}_{\gamma-1}^{-1}(v))$.

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 with the Boltzmann statistics. Thus, to keep the gradient structure, and hence the sound thermodynamical modelling, in the case of Fermi–Dirac statistics we have to write the recombination terms not as polynomials in the densities n_1, \dots, n_I but as linear combinations of the driving forces, as was done already in [AGH02]. For the exponential Boltzmann statistics this was equivalent, but for non-exponential statistics only the latter is consistent with the gradient structure and the Onsager principle, see (3.5).

As an example consider the two-species model for electrons and holes, namely $\mathbf{n} = (n, p)$. Independent of the statistics, the reaction terms have the form

$$\begin{pmatrix} \dot{n} \\ \dot{p} \end{pmatrix} = k(n, p, \theta) \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \begin{pmatrix} \eta_n \\ \eta_p \end{pmatrix} = k(n, p, \theta)(\eta_n + \eta_p) \begin{pmatrix} 1 \\ 1 \end{pmatrix} = -k(n, p, \theta)r(n, p, \theta) \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$\text{with } r(n, p, \theta) = k_B \left(f'_n(n/n^\circ(\theta)) + f'_p(p/p^\circ(\theta)) - \frac{1}{\theta}(E_n(\theta) - E_p(\theta)) \right),$$

see (3.5). Thus, for the Boltzmann case we obtain the polynomial form $r(n, p, \theta) = k_B(np - N(\theta)^2)$ for a suitable function N . For general statistics r cannot be simplified and the full form has to be used.

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