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Thermodynamic design of energy models of semiconductor devices

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Abstract

In this preprint a system of evolution equations for energy models of a semiconductor device is derived on a deductive way from a generally accepted expression for the free energy. Only first principles like the entropy maximum principle and the principle of partial local equilibrium are applied. Particular attention is paid to include the electrostatic potential self-consistently. Dynamically ionized trap levels and models with carrier temperatures are regarded. The system of evolution equations is compatible with the corresponding entropy balance equation that contains a positively definite entropy production rate.

1 Introduction

There is a large variety of energy models for semiconductor devices. G. Wachutka proposed a rigorous thermodynamic model [20] (or [21]). His model is based on the usual state equations and continuity equations for the carrier densities of electrons and holes, n_1 and n_2, and on the conservation of the total energy expressed by the equation $\partial_t \overline{u} + \nabla \cdot j_{\overline{u}} = 0$ for the density $\overline{u}$ and the current density $j_{\overline{u}}$ of this total energy. Neither he has chosen, however, $\overline{u}$ as an independent state variable nor he has given state equations for all out of three independent state variables of his model. Instead of doing so he has used differential relations for $\overline{u}$ and general thermodynamic relations for $j_{\overline{u}}$ and transformed the energy balance equation into a heat flow equation $C\partial_t T - \nabla \cdot (\kappa \nabla T) = H$, the discussion of which was the main subject of those papers. Meanwhile the heat flow equation with the description of the source term H is well established, the discussion about its relation to the conservation law of energy has been going on. H. Brand and S. Selberherr [6] have derived the heat flow equation from the assumption that the density of total energy as a function of the carrier densities and of the density s of entropy would be a thermodynamic potential. This assumption, however, is wrong - at least in the naive setting in which it was applied. To see this one considers two states $'$ and $''$ with $n_2' \equiv n_2''$, $s' \equiv s''$, but $n_1'' - n_1'$ differs from zero only on a (small) ball $B \subset \Omega$ of the domain which is occupied by the device. Then all other state variables should also differ only in B, but the electrostatic potentials, Ψ' and Ψ'', differ also outside the ball. To our knowledge U. Lindefelt [15] was the first who observed a certain inconsistency of Wachutka's arguments which are based on the conservation of the total energy. Indeed, the semiconductor device also in its simplified model is not a closed system, since the external electrostatic field represented by the bias voltages at Dirichlet contacts or gate contacts performs work in the device. U. Lindefelt and also J. E. Parrott [17] derived an energy balance equation by applying the moment method to the Boltzmann equation. Considering the moments and the kinetically defined entropy of particularly parametrized distribution functions near a local equilibrium and using a first-order approximation they get a system of evolution equations. The density of energy which they balance is not the density of total energy of a system of charged particles with a self-consistent electrostatic potential.

Mathematical simulation of semiconductor devices yields another point of view than physical modelling, since all quantities must be expressed more or less explicitly by the independent state variables which are determined by the system of evolution equations. Moreover the mathematical methods to solve a system of evolution equations are, in general, much less perfect than the methods of nature in the real world. Often some useful information already hidden in the system of evolution equations can be more easily obtaind from additional dependent state variables. Stimulated by the ideas of H. Gajewski and K. Gröger [10], which have applied tools of convex analysis and a free energy as a Ljapunov function in the analysis of the drift-diffusion model, G. Albinus [2] has tried to define the total energy as the sum of internal energy and of electrostatic energy and to consider the entropy as a function of the carrier densities and of this total energy. As a result of this construction nonlocal conjugate variables to n_1 and n_2 arise (cf. [3],Th. 2.1), which are quite unusual in the field and which are, moreover, rather inconvenient from the mathematical point of view.

These observations stimulated us to ask for a thermodynamically correct description of systems with a nonlocal interaction like the electrostatic one. In this paper we give an answer to this question. Based on the expression for the density of free energy (cf. [19], chap. VIII) we derive a system of evolution equations on a deductive way. Thereby we only apply first principles like the entropy maximum principle and the principle of partial local equilibrium. Moreover we assume that the total energy is the sum of the internal energy and of the electrostatic energy. The last assumption is justified by the fact that in simulation practice it is assumed that the dielectric permittivity does not depend on the temperature and that the heat capacity does not depend on the electric field.

We also dicuss the case of carrier temperatures. Although G. Wachutka [22] has already described the system of evolution equations, the explicite description of the system with carrier temperatures and its thermodynamic background given in Sect. 6 and Sect. 7 are new to our knowledge. We include also a species of trap levels of donor type which are dynamically ionized. It seems to us particularly interesting to see in the concrete model of a semiconductor device that some thermodynamic concepts are not defined and some relations do not hold for general states $(n_0, n_1, n_2, T, T_1, T_2)$

which are called states of partial local equilibrium. The choice of the densities of internal energy and of entropy in these states, in particular, is justified by the facts that

- the Lagrange method for the realization of the entropy maximum principle combined with the principle of partial local equilibrium yields state equations generally accepted in simulation practice,
- the thermodynamic forces and fluxes derived on the base of the description of states of equilibrium and on the base of the condition of positive entropy production also agree with the equations used in simulation practice, and
- the choice of system of evolution equations (in each stage of the deduction) is compatible with the corresponding entropy balance equation having a positively definite expression for the entropy production.

2 Notation and Assumptions

We consider simple, but generally accepted models of a semiconductor. The semiconductor is considered as a system which consists of several subsystems, the subsystem of electrons in the conduction band, the subsystem of holes in the valence band and the lattice. The lattice is described by a heat capacity (per unit volume) c_L, by a dielectric permittivity ε, by a doping profile d which is a fixed density of completely ionized donors or acceptors and by a fixed density N_D of donor like trap levels which are dynamically ionized, D^+, or not, $D^\times$. The ionization and dissoziation are described as chemical reactions, $D^\times \rightleftarrows D^+ + \ominus$ or $D^\times + \oplus \rightleftarrows D^+$. The ionization energy of the electrons in the traps is denoted by E_0, which is a value between the band edges E_2 and E_1 of the valence band and the conduction band. In general we admit that each subsystem has its own temperature, T_1, T_2, and T. In the following three sections we consider, however, the case of coinciding temperatures, $T_1 \equiv T_2 \equiv T$. In contrast to general states $(\mathbf{n}, \mathbf{T}) \equiv (n_0, n_1, n_2, T, T_1, T_2)$ of partial local eqilibrium we call such states $(\mathbf{n}, T)$ states of partial local thermal eqilibrium.

The electrostatic interaction of the subsystems and an external electric field are described in Sect. 7 as a boundary value problem $\Pi^{\omega}_{\Gamma_D}(n_2 + N_D - n_0 - n_1)$ for the Poisson equation $-\nabla \cdot (\varepsilon \nabla \Psi) = d + n_2 + N_D - n_0 - n_1$ with the solution $\Psi = \mathbf{P}^{\omega}_{\Gamma_D}(n_2 + N_D - n_0 - n_1)$. We introduce the 'charge numbers' $q_2 = -q_0 = -q_1 = 1$. For the purpose of simulation practice it can be assumed that the dielectric permittivity ε does not depend on the temperature and that the heat capacity does not depend on the electric field strength. Because of such assumptions (or simplifications) we can and we do assume that the free energy is a sum of the electrostatic energy $U^{\omega}_{\Gamma_D}(n_2 + N_D - n_0 - n_1)$ and of an 'internal free energy'. Our basic assumption is that the internal free energy of the whole system in a state of partial local thermal equilibrium is given by the density

$$\begin{aligned} f(\mathbf{n},T) =& c_L(T - T\log T) - \sum_{j=0}^{2} q_j n_j E_j(T) \\ & + T\log\left[\left(\frac{n_0}{2(N_D-n_0)}\right)^{n_0}\left(\frac{N_D-n_0}{N_D}\right)^{N_D}\right] \\ +T & \sum_{l=1}^{2}\left[n_l\mathcal{F}_{\alpha_l-1}^{-1}\left(\frac{n_l}{M_l(T)T^{\alpha_l}}\right) - T^{\alpha_l}M_l(T)\mathcal{F}_{\alpha_l}\circ\mathcal{F}_{\alpha_l-1}^{-1}\left(\frac{n_l}{M_l(T)T^{\alpha_l}}\right)\right] \end{aligned} \tag{2.1}$$

with the state densities $M_i(T)T^{\alpha_i}$ $(i = 1, 2)$. The indices α_i of the Fermi integrals are usually $3/2$ (parabolic band structure), but we allow indices $\alpha_i > 1$. In simulation practice one usually assumes that the effective masses of electrons and holes, which contribute to the factors M_i, and the band gap $E_g = E_1 - E_2$ depend on the temperature. Therefore we admit material laws $E_i(T)$ and $M_i(T)$ in general. The Fermi integral $\mathcal{F}_\gamma$ with the index $\gamma > -1$ is defined by

$$\mathcal{F}_\gamma(y) = \frac{1}{\Gamma(\gamma+1)}\int_0^\infty \frac{z^\gamma}{1+\exp(z-y)}\,dz\ ,$$

such that its derivative is $\mathcal{F}_\gamma' = \mathcal{F}_{\gamma-1}$ $(\gamma > 0)$. One can easily switch to the case of Boltzmann statistics simply by substituting all Fermi integrals $\mathcal{F}_\gamma$ by the exponential function exp and the inverse functions $\mathcal{F}_\gamma^{-1}$ by log. This switching is often quite helpful, because the expressions become much simpler in general. On the other hand the structure of the formulas becomes more clearly in the case of Fermi-Dirac statistics.

It is well known that the free energy (per unit volume) as a function of the particle densities and temperature is a thermodynamic potential which contains much information of the physical system. In contrast to the usual (irreversible) thermodynamics where (local) equilibrium states are studied the free energy here is defined for states of partial local thermal equilibrium which is a partial equilibrium with respect to the densities.

In the next four sections we consider systems without electrostatic interaction. In the next three sections we consider a system in local thermal equilibrium that has a density of free energy defined by (2.1). In Sect. 6 we admit carrier temperatures T_i for the electrons in the conduction band $(i = 1)$ and for the holes in the valence band $(i = 2)$, which may differ from the lattice temperature T (hot electrons). In Sect. 7 the electrostatic interaction is included, the energy models of semiconductors with and without hot electrons are presented as the result of a purely thermodynamic deduction from the density of the free energy (2.1). In Sect. 8 the preceding arguments and results are specified for the case that the Boltzmann statistics can be applied to the carriers.

Notice that we use a convenient scaling such that the physical quantities become dimensionless. Sometimes it will be sufficient to consider only spatially homogeneous states. In these cases the densities n_i, d, N_D and the temperatures are constant or functions of time only, and the material laws do not excplicitly depend on the spatial coordinates. In general, however, the material laws may also explicitly depend on the spatial coordinates, but this dependence will usually not be indicated.

3 The Entropy Maximum Principle

For the readers convenience we compile here some short notation which will be useful throughout the paper.

$$\begin{aligned}
\mathcal{P}_i &\equiv M_i(T)T^{\alpha_i}\mathcal{F}_{\alpha_i}\circ\mathcal{F}^{-1}_{\alpha_i-1}\left[\frac{n_i}{M_i(T)T^{\alpha_i}}\right] ,\\
\mathcal{Q}_i &\equiv \frac{n_i^2}{M_i(T)T^{\alpha_i}\mathcal{F}_{\alpha_i-2}\circ\mathcal{F}^{-1}_{\alpha_i-1}\left[\frac{n_i}{M_i(T)T^{\alpha_i}}\right]} ,\\
\mathcal{D}_i &\equiv \mathcal{P}_i-\mathcal{Q}_i = M_i(T)T^{\alpha_i}\left[\mathcal{F}_{\alpha_i}(z)-\frac{\mathcal{F}_{\alpha_i-1}(z)^2}{\mathcal{F}_{\alpha_i-2}(z)}\right]_{z=\mathcal{F}^{-1}_{\alpha_i-1}\left[\frac{n_i}{M_i(T)T^{\alpha_i}}\right]} ,
\end{aligned}$$

and $L_i(T)\equiv T\partial_T\left[\log M_i(T)\right]\quad(i=1,2)$. Notice that

$$\mathcal{D}_i > -\frac{1}{\alpha_i}M_i(T)T^{\alpha_i}\mathcal{F}_{\alpha_i}(z) .$$

The densities of the entropy and of the energy of a system with the density (2.1) of the free energy are defined by

$$\begin{aligned}
s = s_f(\mathbf{n},T) &= -\,\partial_T f(\mathbf{n},T)\\
&= c_L\log T+\sum_{j=0}^{2}q_jn_jE_j'(T)-\log\left[\left(\frac{n_0}{2(N_D-n_0)}\right)^{n_0}\left(\frac{N_D-n_0}{N_D}\right)^{N_D}\right]\\
&\quad+\sum_i\left[(\alpha_i+1+L_i(T))\,\mathcal{P}_i-n_i\mathcal{F}^{-1}_{\alpha_i-1}\left(\frac{n_i}{M_i(T)T^{\alpha_i}}\right)\right]
\end{aligned}\tag{3.1}$$

and

$$\begin{aligned}
u = u_f(\mathbf{n},T) &= f(\mathbf{n},T)-T\partial_T f(\mathbf{n},T) \;=\; f+Ts\\
&= c_LT-\sum_{j=0}^{2}q_jn_j[E_j(T)-TE_j'(T)]+T\sum_{l=1}^{2}\left[\alpha_l+L_l(T)\right]\mathcal{P}_l ,
\end{aligned}\tag{3.2}$$

where the prime denotes the derivative with respect to the only argument T.

Proposition 3.1 *(Entropy maximum principle) If the heat capacity of the system is positive, i.e. if*

$$\begin{aligned} C \equiv & \partial_T u_f = -T\partial_T^2 f = -T\partial_T s_f \\ = & c_L + \sum_{j=0}^{2} q_j n_j T E_j''(T) + \sum_{l=1}^{2} \left[(\alpha_l + [T L_l(T)]') \mathcal{P}_l + (\alpha_l + L_l(T))^2 \mathcal{D}_l \right] \ > \ 0 \ , \end{aligned}$$

the entropy $S = \int s_f(\mathbf{n}, T)\, d\Omega$ *realizes its maximum under the constraints*

$$U_0 = \int u_f(\mathbf{n}, T)\, d\Omega \qquad \text{and} \quad Q = \int (n_2 - n_1 - n_0)\, d\Omega$$

at one of the equilibrium states which are characterized by the equilibrium conditions $T = 1/\lambda \equiv \theta$ *and*

$$\xi = -q_i \partial_{n_i} \left[\frac{1}{\theta} u_f(\mathbf{n}, \theta) - s_f(\mathbf{n}, \theta) \right] = -q_i \frac{E_i(\theta)}{\theta} - \begin{cases} \log \frac{2(N_D - n_0)}{n_0} & (i = 0) \\ q_i \mathcal{F}_{\alpha_i - 1}^{-1} \left[\frac{n_i}{M_i(\theta)\theta^{\alpha_i}} \right] & (i = 1, 2) \end{cases} .$$

The proof is a straightforward application of the Lagrange method. The constants λ and ξ are the Lagrange multipliers of the two constraints. Their values and thus the equilibrium densities

$$\overline{n}_0 = N_D \frac{2}{2 + \exp \frac{E_0(\theta) - \zeta}{\theta}} \quad \text{and} \quad \overline{n}_i = M_i(\theta) \theta^{\alpha_i} \mathcal{F}_{\alpha_i - 1} \left[-q_i \frac{\zeta - E_i(\theta)}{\theta} \right] \qquad (i = 1, 2) \ ,$$

($\xi \equiv \zeta/\theta$) are determined by the constraints, which form a system of two nonlinear equations.

Remark 3.1 *The derivatives of* E_i *and* M_i *with respect to* T *in the expressions* (3.1) *and* (3.2) *naturally occur if one starts from the free energy* (2.1)*. They guarantee that the temperature is constant in the equilibrium states defined by the entropy maximum principle. If these terms had been omitted the temperature* T *would neither coincide with* $1/\lambda$ *nor be constant in equilibrium states. Is there a plausible physical interpretation of these terms?*

Remark 3.2 *For the states of partial local thermal equilibrium we introduce state variables* ζ_i *according to the structure of the equilibrium densities. In this sense the state equations*

$$n_0 = N_D \frac{2}{2 + \exp \frac{1}{T} \left[E_0(T) - \zeta_0 \right]} \quad \text{and} \quad n_i = M_i(T) T^{\alpha_i} \mathcal{F}_{\alpha_i - 1} \left(\frac{q_i}{T} \left[E_i(T) - \zeta_i \right] \right)$$

($i = 1, 2$) *are a stringent consequence of the expression of the free energy. As long as we neglect the electrostatic interaction between the carriers, we can not distinguish electrochemical and chemical potentials. Let us call the* ζ_i *electrochemical potentials, since we have already regarded the charge of the carriers and traps.*

Remark 3.3 *Notice that the identity* $\partial_T u_f = T\partial_T s_f$ *reflects the principle of local thermal equilibrium of the irreversible thermodynamics. The heat capacity of the system is positive if the estimate*

$$c_L + \sum_{j=0}^{2} q_j n_j T E_j'' \quad > \quad \sum_{l=1}^{2} \left(\frac{1}{\alpha_l} L_l(T)^2 + L_l(T) - T L_l(T)' \right) M_l(T) T^{\alpha_l} \mathcal{F}_{\alpha_l}$$

holds. This estimate is satisfied in the model case in which the band edges E_i *and the functions* M_i *(i.e. the effective masses) do not depend on the temperature. The estimate is checked in the Appendix for material laws which are used in simulation practice.*

Remark 3.4 *A glance at* (3.1) *suggests that the quantities*

$$P_i := [\alpha_i + 1 + L_i(T)] \left. \frac{\mathcal{F}_{\alpha_i}(z)}{\mathcal{F}_{\alpha_i - 1}(z)} \right._{z = \frac{q_i}{T}[E_i(T) - \zeta_i]} + \frac{q_i}{T} \left(\zeta_i - [E_i(T) - T E_i'(T)] \right)$$

($i = 1, 2$) are the entropies per carrier. These quantities will play a role in the current equations, where they also justify the name 'thermoelectric power'.

The following proposition is closely related to the entropy maximum principle.

Proposition 3.2 *If the heat capacity* C *is positive, the implicitly defined function* $\overline{s}(\mathbf{n}, u) := s_f(\mathbf{n}, T)$ *with* $u = u_f(\mathbf{n}, T)$ *is a thermodynamic potential. Its first-order partial derivatives are the conjugate variables*

$$\partial_u \overline{s} = \frac{\partial_T s_f}{C} = \frac{1}{T} =: \tau$$

and

$$\partial_{n_i} \overline{s} = \partial_{n_i} \left(s_f - \frac{1}{T} u_f \right) \quad = \quad q_i \frac{\zeta_i}{T} \equiv: q_i \xi_i \qquad (i = 0, 1, 2) \; . \tag{3.3}$$

The negative conjugate potential of $\overline{s}$ *is the potential*

$$\begin{aligned} \overline{h}(\xi_0, \xi_1, \xi_2, \tau) =& s_f(\mathbf{n}, T) - \frac{1}{T} u_f(\mathbf{n}, T) - \sum_{j=0}^{2} q_j n_j \xi_j \\ =& c_L(\log T - 1) + N_D \left[\xi_0 - \frac{1}{T} E_0(T) + \log\left(2 + e^{E_0(T)/T - \xi_0}\right) \right] \\ & + \sum_{l=1}^{2} M_l(T) T^{\alpha_l} \mathcal{F}_{\alpha_l} \left[q_l \left(\frac{1}{T} E_l(T) - \xi_l \right) \right] \qquad (\tau \equiv 1/T) \; . \end{aligned}$$

In the following the state variable ξ_0 will be considered as a fixed parameter, because the occupied traps are localized electrons. Thus let us denote the function $\overline{h}(\xi_0, ., ., .) \equiv: h$. It will be, moreover, convenient to stick to the variable T instead of the correct conjugate variable τ. Therefore we denote $h(., ., \tau) \equiv: H(., ., T)$ and notice that $\partial_\tau h(., ., \tau) = -T^2 \partial_T H(., ., T)$. The first-order partial derivatives of h are

$$\partial_{\xi_i} H(\xi_1, \xi_2, T) = -\, q_i M_i(T) T^{\alpha_i} \mathcal{F}_{\alpha_i - 1} \left[q_i \left(E_i(T)/T - \xi_i \right) \right] \qquad (i = 1, 2)$$

and

$$\begin{aligned} -T^2 \partial_T H(., ., T) = &- c_L T - [E_0(T) - T E_0'(T)] N_D \frac{2}{2 + \exp\left[E_0(T)/T - \xi_0\right]} \\ &+ \sum_{l=1}^{2} q_l [E_l(T) - T E_l'(T)] M_l(T) T^{\alpha_l} \mathcal{F}_{\alpha_l - 1} \left[q_l \left(\frac{1}{T} E_l(T) - \xi_l \right) \right] \\ &- T \sum_{l=1}^{2} [\alpha_l + L_l(T)] M_l(T) T^{\alpha_l} \mathcal{F}_{\alpha_l} \left[q_l \left(\frac{1}{T} E_l(T) - \xi_l \right) \right] \ . \end{aligned}$$

Remember that the quantities $T^2 \partial_T H(., ., T) = u_f(\mathbf{n}, T)$ coincide, although the functions on both sides are quite different. The 3×3-matrix $d^2 h$ of second-order partial derivatives reads

$$\begin{pmatrix} A_1^{1/2} & 0 & 0 \\ 0 & A_2^{1/2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & A_1^{-1/2} F_1 \\ 0 & 1 & A_2^{-1/2} F_2 \\ A_1^{-1/2} F_1 & A_2^{-1/2} F_2 & A_L \end{pmatrix} \begin{pmatrix} A_1^{1/2} & 0 & 0 \\ 0 & A_2^{1/2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

with $A_i = M_i(T) T^{\alpha_i} \mathcal{F}_{\alpha_i - 2} > 0$ $(i = 1, 2)$,

$$F_i = M_i(T) T^{\alpha_i} \left[q_i T \left(L_i(T) + \alpha_i \right) \mathcal{F}_{\alpha_i - 1} - \left(E_i - T E_i' \right) \mathcal{F}_{\alpha_i - 2} \right] \ ,$$

and

$$\begin{aligned} A_L = &c_L T^2 + T^3 \sum_{j=0}^{2} q_j n_j E_j''(T) + \frac{1}{N_D} [E_0(T) - T E_0'(T)]^2 n_0 (N_D - n_0) \\ &+ \sum_{l=1}^{2} M_l(T) T^{\alpha_l} \left[T^2 \left(\alpha_l + [T L_l(T)]' + [\alpha_l + L_l(T)]^2 \right) \mathcal{F}_{\alpha_l} \right. \\ &\left. -2 q_l [E_l(T) - T E_l'(T)] T [\alpha_l + L_l(T)] \mathcal{F}_{\alpha_l - 1} + [E_l(T) - T E_l'(T)]^2 \mathcal{F}_{\alpha_l - 2} \right] \ . \end{aligned}$$

Notice that the identity

$$A_L - \sum_{l=0}^{2} F_l^2 / A_l \equiv C T^2 + \frac{1}{N_D} [E_0(T) - T E_0'(T)]^2 n_0 (N_D - n_0)$$

hold.

Proposition 3.3 *If the heat capacity C is positive, the matrix d^2h is positively definite.*

If for a fixed ξ_0 the heat capacity is positive on a convex domain of states $(\xi_1, \xi_2, 1/T)$, the function h is a strictly convex with the partial derivatives

$$\partial_{\xi_i} h = -q_i n_i \qquad (i = 1, 2) \ , \quad \text{and} \quad \partial_\tau h = -u \ .$$

The convexity of h means, mathematically spoken, that the operator $(-\xi_1, \xi_2, \tau) \mapsto (n_1, n_2, u)$ is strictly monotone, i.e.

$$-(n_1' - n_1'')(\xi_1' - \overline{\xi}_1'') + (n_2' - n_2'')(\xi_2' - \xi_2'') + (u' - u'')(\tau' - \tau'') < 0$$

for different triples $(\xi_1^\iota, \xi_2^\iota, \tau^\iota)$ and the corresponding conjugate triples.

4 Thermodynamic Forces in homogeneous States

Knowing the equilibrium states of the system we are going to define thermodynamic forces that drive a state of partial local thermal equilibrium into the corresponding equilibrium. In this section we study the transition from homogeneous states of partial equilibrium into the corresponding equilibrium. The realization of the maximum entropy principle by means of the Lagrange method suggests that the differences of the reduced potentials ξ_i $(i = 0, 1, 2)$ are the driving forces for the exchange of electrons or holes between the subsystems. The process of assimilation of the reduced potentials to each other is derived from the mass action law.

The exchange of electrons or holes between the subsystems is realized by three pairs '0', '1', and '2' of 'chemical reactions',

$$\ominus + \oplus \leftrightarrows \emptyset + E_1 - E_2 \ , \quad D^\times + \oplus \leftrightarrows D^+ + E_0 - E_2 \ , \quad \text{or} \quad D^\times \leftrightarrows D^+ + \ominus - (E_1 - E_0) \ ,$$

respectively. The rates of recombination, thermal generation, dissociation, or ionization are $\rho_0 n_1 n_2$, γ_0, $\rho_1 n_0 n_2$, $\gamma_1(N_D - n_0)$, $\rho_2(N_D - n_0)n_1$, and $\gamma_2 n_0$. For any state $(\mathbf{n}, T)$ with the corresponding potentials ξ_i there are uniquely determined solutions $\overline{\xi}^0$, $\overline{\xi}^1$, and $\overline{\xi}^2$ of the corresponding equations

$$\begin{aligned}
N_2\mathcal{F}_{\alpha_2-1}(\varepsilon_2 - \xi) - N_1\mathcal{F}_{\alpha_1-1}(\xi - \varepsilon_1) &= N_2\mathcal{F}_{\alpha_2-1}(\varepsilon_2 - \xi_2) - N_1\mathcal{F}_{\alpha_1-1}(\xi_1 - \varepsilon_1) \\
&= n_2 - n_1 \ , \\
N_2\mathcal{F}_{\alpha_2-1}(\varepsilon_2 - \xi) - \frac{2N_D}{2 + \exp(\varepsilon_0 - \xi)} &= N_2\mathcal{F}_{\alpha_2-1}(\varepsilon_2 - \xi_2) - \frac{2N_D}{2 + \exp(\varepsilon_0 - \xi_0)} \\
&= n_2 - n_0 \ , \\
N_1\mathcal{F}_{\alpha_1-1}(\xi - \varepsilon_1) + \frac{2N_D}{2 + \exp(\varepsilon_0 - \xi)} &= N_1\mathcal{F}_{\alpha_1-1}(\xi_1 - \varepsilon_1) + \frac{2N_D}{2 + \exp(\varepsilon_0 - \xi_0)} \\
&= n_1 + n_0 \ ,
\end{aligned}$$

where the short notation $N_i :\equiv M_i(T)T^{\alpha_i}$ and $\varepsilon_i :\equiv E_i(T)/T$ $(i = 0,1,2)$ has been used. The densities $\overline{n}_i^k$ and $\overline{n}_j^k$ which correspond to this reduced potential $\overline{\xi}^k$ $(i \neq k$, $j \neq k)$ represent the equilibrium of the recombination and generation processes 'k', i.e. e.g. $\overline{\rho}_0\overline{n}_1^0\overline{n}_2^0 = \overline{\gamma}_0$. The assumption $\rho_k = \overline{\rho}_k$ and $\gamma_k = \overline{\gamma}_k$, which mean a linearization-like approximation, permit us to write the net recombination rate in the form $\rho_0 n_1 n_2 - \gamma_0 = \rho_0\left(n_1 n_2 - \overline{n}_1^0\overline{n}_2^0\right)$. Notice that the quantities $n_1 - \overline{n}_1^0$, $n_2 - \overline{n}_2^0$, $n_1 n_2 - \overline{n}_1^0\overline{n}_2^0$, and $\xi_1 - \xi_2$ have all the same sign, because

$$N_2\left[\mathcal{F}_{\alpha_2-1}\left(\varepsilon_2 - \xi_2\right) - \mathcal{F}_{\alpha_2-1}\left(\varepsilon_2 - \overline{\xi}_2^1\right)\right] = N_1\left[\mathcal{F}_{\alpha_1-1}\left(\xi_1 - \varepsilon_1\right) - \mathcal{F}_{\alpha_1-1}\left(\overline{\xi}_2^1 - \varepsilon_1\right)\right]$$

such that $-\xi_2 > -\overline{\xi}^0$ if and only if $\xi_1 > \overline{\xi}^0$. Thus the net recombination rate can be written as

$$R_0 = \rho_0\left(n_1 n_2 - \overline{n}_1^0\overline{n}_2^0\right) = r_0(\mathbf{n},T)\exp\left[\frac{1}{T}(E_2(T) - E_1(T))\right]\left[\exp\left(\xi_1 - \xi_2\right) - 1\right]$$

with a nonnegative material law r_0. Analogous arguments yield

$$R_i = r_i(\mathbf{n},T)\exp\left[-\frac{q_i}{T}(E_{i^*}(T) - E_0(T))\right]\left[\exp\left(q_i\xi_{i^*} - q_i\xi_0\right) - 1\right] \qquad (i = 1,\, 2)$$

with the notation $i^* := i - (-1)^i$ and with nonnegative material laws r_1 and r_2 .

We assume that the evolution of homogeneous states of partial local thermal equilibrium is described by the following system of differential equations,

$$\begin{aligned} \dot{n}_0 &= R_2 - R_1\ , \\ \dot{n}_i &= -R_0 - R_{i^*} \qquad (i = 1,2)\ , \\ \dot{T}\partial_T u_f &= -\sum_{j=0}^{2}\dot{n}_j\partial_{n_j}u_f = \sum_{\iota=0}^{2} R_\iota U^\iota\ , \end{aligned} \tag{4.1}$$

where the short notation

$$\begin{aligned} U^0 \equiv \partial_{n_1}u_f + \partial_{n_2}u_f &= E_1 - TE_1' + TL_1Q_1/n_1 - E_2 + TE_2' + TL_2Q_2/n_2\ , \\ U^1 \equiv \partial_{n_2}u_f + \partial_{n_0}u_f &= E_0 - TE_0' - E_2 + TE_2' + TL_2Q_2/n_2\ , \end{aligned}$$

and

$$U^2 \equiv \partial_{n_1}u_f - \partial_{n_0}u_f = E_1 - TE_1' + TL_1Q_1/n_1 - E_0 + TE_0'$$

has been used. The quantities S^ι as well as $\widetilde{U}^\iota$ and $\widetilde{S}^\iota$ in Sect. 6 below are defined analogously with s_f, $\widetilde{u}_f$, and $\widetilde{s}_f$, respectively. The fourth equation of the system describes the conservation of energy.

The entropy $s = s_f[\mathbf{n}, T]$ of a solution of the system (4.1) satisfies the entropy balance equation

$$\begin{aligned} \dot{s} &= \sum_{j=0}^{2} \dot{n}_j \partial_{n_j} s_f + \dot{T}\partial_T s_f = -\sum_{\iota=0}^{2} R_\iota S^\iota + \frac{1}{T}\dot{T}\partial_T u_f = \sum_{\iota=0}^{2} R_\iota \left(\frac{1}{T}U^\iota - S^\iota\right) \\ &= r_0 \exp\left[\frac{1}{T}\left(E_2(T) - E_1(T)\right)\right] (\xi_1 - \xi_2) \left[\exp\left(\xi_1 - \xi_2\right) - 1\right] \\ &+ \sum_{l=1}^{2} r_l \exp\left[-\frac{q_l}{T}\left(E_{l^*}(T) - E_0(T)\right)\right] (q_l\xi_{l^*} - q_l\xi_0) \left[\exp\left(q_l\xi_{l^*} - q_l\xi_0\right) - 1\right] \end{aligned} \tag{4.2}$$

The positive definiteness of the entropy production is an argument for the right choice of the evolution equations!

5 Thermodynamic Forces in inhomogeneous States

The existence of fluxes of particles and of energy in inhomogeneous states of partial local thermal equilibrium driven by the gradients of the conjugate variables ξ_1, ξ_2, and τ according to

$$\begin{pmatrix} j_{n_1} \\ j_{n_2} \\ j_u \end{pmatrix} = \begin{pmatrix} \mathbf{D}_{11} & \mathbf{D}_{12} & \mathbf{D}_{1u} \\ \mathbf{D}_{21} & \mathbf{D}_{22} & \mathbf{D}_{2u} \\ \mathbf{D}_{u1} & \mathbf{D}_{u2} & \mathbf{D}_{uu} \end{pmatrix} \cdot \begin{pmatrix} -\nabla\xi_1 \\ \nabla\xi_2 \\ \nabla\tau \end{pmatrix} \equiv \mathbf{D} \cdot \begin{pmatrix} -\nabla\xi_1 \\ \nabla\xi_2 \\ \nabla\tau \end{pmatrix}$$

can be motivated by a decomposition of the whole device into small cells which exchange particles and energy. The strict convexity of the function h can be applied to derive the positive definiteness of the coefficient matrix. To this aim the domain $\Omega \subset R^3$ which is occupied by the system is decomposed into small cells ι with individual values ξ_1^ι, ξ_2^ι, and τ^ι of the independent state variables. Differences of these values in neighboured cells causes an exchange of carriers and energy between these cells. The rate of the exchange is determined by the 'permeability' or 'conductivity' of the interfaces between neighboured cells and the exchange must be accompanied with a growth of entropy. In the limit of vanishing cell volume the differential law arises formally. We do not need this motivation, since the positive definiteness of the coefficient matrix follows from the following proposition in connection with the thermodynamic condition that the entropy production has to be positive. The elements of the coefficient matrix are state variables.

Proposition 5.1 *Let* $(\mathbf{n}, T)$ *be a solution of the following system of evolution equa-*

tions

$$
\begin{aligned}
\dot{n}_0 &= R_2 - R_1 \ , \\
\dot{n}_i + \nabla \cdot \jmath_{n_i} &= -R_0 - R_{i^*} \qquad (i = 1, 2) \ , \\
\dot{T}\partial_T u_f + \nabla \cdot \jmath_u &= \sum_{\iota=0}^{2} R_\iota U^\iota + \sum_{l=1}^{2} \partial_{n_l} u_f \nabla \cdot \jmath_{n_l}
\end{aligned}
\tag{5.1}
$$

The density of entropy $s = \overline{s}_f[\mathbf{n}, T]$ satisfies the entropy balance equation

$$
\begin{aligned}
\dot{s} + \nabla \cdot \jmath_s = (\xi_1 - \xi_2)\, R_0 + \sum_{l=1}^{2} q_l \,(\xi_{l^*} - \xi_0)\, R_l \\
+ \begin{pmatrix} -\nabla\xi_1 \\ \nabla\xi_2 \\ \nabla\tau \end{pmatrix} \cdot \mathbf{D} \cdot \begin{pmatrix} -\nabla\xi_1 \\ \nabla\xi_2 \\ \nabla\tau \end{pmatrix}
\end{aligned}
\tag{5.2}
$$

with the entropy flux

$$
\jmath_s = -\xi_1 \jmath_{n_1} + \xi_2 \jmath_{n_2} + \frac{1}{T}\jmath_u \ . \tag{5.3}
$$

*Proof.*An immediate evaluation shows

$$
\begin{aligned}
\dot{s} &= \dot{\mathbf{n}} \cdot \partial_{\mathbf{n}} s_f + \dot{T}\partial_T s_f = \dot{\mathbf{n}} \cdot \partial_{\mathbf{n}} s_f + \frac{1}{T}\dot{T}\partial_T u_f \\
&= \sum_{\iota=0}^{2} R_\iota \left(\frac{1}{T}U^\iota - S^\iota\right) + \sum_{l=1}^{2} \partial_{n_l} \left(\frac{1}{T}u_f - s_f\right) \nabla \cdot \jmath_{n_l} - \frac{1}{T}\nabla \cdot \jmath_u \\
&= R_0(\xi_1 - \xi_2) + \sum_{l=1}^{2} q_l \left[R_l(\xi_{l^*} - \xi_0) - \xi_l \nabla \cdot \jmath_{n_l}\right] - \tau \nabla \cdot \jmath_u \ .
\end{aligned}
$$

The divergence terms provide the divergence of the entropy current density and the part of the entropy production rate due to the current densities. □

We want to discuss the coefficient matrix in some detail, because some general conclusions can be drawn. It will be convenient to write the equations for the current densities in the form

$$
\begin{pmatrix} \begin{pmatrix} \jmath_{n_1} \\ \jmath_{n_2} \end{pmatrix} \\ \jmath_u \end{pmatrix} \equiv \begin{pmatrix} \mathbf{j} \\ \jmath_u \end{pmatrix} = \begin{pmatrix} \mathbf{D}_c & \mathbf{A} \\ \mathbf{B} & \mathbf{D}_\tau \end{pmatrix} \cdot \begin{pmatrix} \begin{pmatrix} -\nabla\xi_1 \\ \nabla\xi_2 \end{pmatrix} \\ \nabla\tau \end{pmatrix} \ .
$$

The requirement that the entropy production has to be positive implies that the coefficient matrix and the block diagonal matrices has to be positively definite, in particular, regular matrices. We write

$$
\begin{pmatrix} \begin{pmatrix} -\nabla\xi_1 \\ \nabla\xi_2 \end{pmatrix} \\ \jmath_u \end{pmatrix} = \begin{pmatrix} \mathbf{D}_c^{-1} & -\mathbf{D}_c^{-1}\mathbf{A} \\ \mathbf{R} & \mathbf{K} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{j} \\ \nabla\tau \end{pmatrix}
$$

with the matrices $\mathbf{R} = \mathbf{B}\mathbf{D}_c^{-1} = (\mathbf{R}_1\ \mathbf{R}_2)$ and $\mathbf{K} = \mathbf{D}_\tau - \mathbf{B}\mathbf{D}_c^{-1}\mathbf{A} = \mathbf{D}_\tau - \mathbf{R}\mathbf{A}$. The current density of entropy turns out to be

$$j_s = \frac{1}{T}\left[(-\zeta_1 \quad \zeta_2)\cdot\mathbf{j} + \mathbf{R}\cdot\mathbf{j} + \mathbf{K}\cdot\nabla\tau\right] \ ,$$

i.e. the matrices $\mathbf{R}_i$ are quasi scalar coefficients

$$\mathbf{R}_i = (TP_i - q_i\zeta_i)\mathbf{I} \ ,$$

which do not contain particular properties of the material, but are determined by the state of the system, in particular, by the entropies per carrier, P_1 or P_2, that were introduced in Rem. 3.4.

Let us introduce a matrix $\mathbf{M}$ instead of the matrix $\mathbf{A}$,

$$\mathbf{D}_c^{-1}\mathbf{A} = \mathbf{R}^T - \mathbf{R}^T + \mathbf{D}_c^{-1}\mathbf{A} \ =: \ \mathbf{R}^T + 2\mathbf{M} \ ,$$

such that

$$\mathbf{j} = \mathbf{D}_c\cdot\left[\begin{pmatrix} -\nabla\xi_1 \\ \nabla\xi_2 \end{pmatrix} + \left(\mathbf{R}^T + 2\mathbf{M}\right)\cdot\nabla\tau\right] \ .$$

Let denote $\mathbf{D}_c^S := \left(\mathbf{D}_c + \mathbf{D}_c^T\right)/2$ and $\mathbf{W} := \sqrt{\left(\mathbf{D}_c^{-1} + \mathbf{D}_c^{T\,-1}\right)/2}$. The entropy production reads

$$\begin{aligned}
\sigma = \begin{pmatrix} \mathbf{j} & \nabla\tau \end{pmatrix}\cdot\begin{pmatrix} \begin{pmatrix} -\nabla\xi_1 \\ \nabla\xi_2 \end{pmatrix} \\ \dot{j}_u \end{pmatrix} \ &= \ \mathbf{j}\cdot\left(\mathbf{D}_c^{-1}\cdot\mathbf{j}\right) - 2\mathbf{j}\cdot(\mathbf{M}\cdot\nabla\tau) + \nabla\tau\cdot(\mathbf{K}\cdot\nabla\tau) \\
&= \mathbf{j}\cdot\left(\mathbf{W}^2\cdot\mathbf{j}\right) - 2\left(\mathbf{W}\cdot\mathbf{j}\right)\cdot\left(\mathbf{W}^{-1}\mathbf{M}\cdot\nabla\tau\right) + (\mathbf{M}\cdot\nabla\tau)\cdot\left(\mathbf{W}^{-2}\mathbf{M}\cdot\nabla\tau\right) \\
&\quad + \nabla\tau\cdot\left[\left(\mathbf{K} - \mathbf{M}^T\mathbf{D}_c^S\mathbf{M}\right)\cdot\nabla\tau\right] \\
&= \left(\mathbf{W}\cdot\mathbf{j} - \mathbf{W}^{-1}\mathbf{M}\cdot\nabla\tau\right)\cdot\left(\mathbf{W}\cdot\mathbf{j} - \mathbf{W}^{-1}\mathbf{M}\cdot\nabla\tau\right) + \nabla\tau\cdot\left[\left(\mathbf{K} - \mathbf{M}^T\mathbf{D}_c^S\mathbf{M}\right)\cdot\nabla\tau\right] \\
&= \left(\mathbf{j} - \mathbf{D}_c^S\mathbf{M}\cdot\nabla\tau\right)\cdot\left[\mathbf{D}_c^{S\,-1}\cdot\left(\mathbf{j} - \mathbf{D}_c^S\mathbf{M}\cdot\nabla\tau\right)\right] + \nabla\tau\cdot\left[\left(\mathbf{K} - \mathbf{M}^T\mathbf{D}_c^S\mathbf{M}\right)\cdot\nabla\tau\right] \\
&= \mathbf{x}\cdot\left(\mathbf{D}_c^S\cdot\mathbf{x}\right) + \nabla\tau\cdot\left[\left(\mathbf{K} - \mathbf{M}^T\mathbf{D}_c^S\mathbf{M}\right)\cdot\nabla\tau\right]
\end{aligned}$$

with the thermodynamic forces

$$\mathbf{x} = \mathbf{D}_c^{S\,-1}\mathbf{D}_c\cdot\left[\begin{pmatrix} -\nabla\xi_1 \\ \nabla\xi_2 \end{pmatrix} + \left(\mathbf{R}^T + 2\mathbf{M} - \mathbf{D}_c^{-1}\mathbf{D}_c^S\mathbf{M}\right)\cdot\nabla\tau\right] \ .$$

We do not see that the model requires or implies the symmetry of the coefficient matrix which maps the thermodynamic forces $-\nabla\xi_1$, $\nabla\xi_2$, and $\nabla\tau$ into the fluxes j_{n_1}, j_{n_2}, and $\dot{j}_u$, but the symmetry seems to be plausible in the absence of magnetism due to kinetic modelling.

In the symmetric case, i.e. if $\mathbf{D}_c = \mathbf{D}_c^T$, $\mathbf{K} = \mathbf{K}^T$, and $\mathbf{M} = 0$, the thermodynamic forces

$$x_i = q_i \nabla \xi_i + (TP_i - q_i\zeta_i)\nabla\tau = -\frac{1}{T}(-q_i\nabla\zeta_i + P_i\nabla T)$$

$(i = 1, 2)$ and $\nabla\tau$ form a basis in the space of thermodynamic forces which decomposes the entropy production into a sum of the entropy production due to the carrier fluxes and of the entropy production due to gradient of temperature. The matrix $\mathbf{K}$ has to be positive definite. The fluxes read in the more detailed version

$$j_u = \sum_{l=1}^{2}(TP_l - q_l\zeta_l)\, j_{n_l} + \mathbf{K}\cdot\nabla\frac{1}{T}$$

and

$$\begin{aligned}
\begin{pmatrix} j_{n_1} \\ j_{n_2} \end{pmatrix} &= -\frac{1}{T}\mathbf{D}_c \cdot \begin{pmatrix} \nabla\zeta_1 + P_1\nabla T \\ -\nabla\zeta_2 + P_2\nabla T \end{pmatrix} \\
&= -\frac{1}{T}\begin{pmatrix} (\mathbf{D}_{11} - \mathbf{D}_{12})\cdot(\nabla\zeta_1 + P_1\nabla T) \\ (\mathbf{D}_{22} - \mathbf{D}_{12}^T)\cdot(-\nabla\zeta_2 + P_2\nabla T) \end{pmatrix} \\
&\quad - \frac{1}{T}\begin{pmatrix} \mathbf{D}_{12} \\ \mathbf{D}_{12}^T \end{pmatrix}\cdot\left[\nabla(\zeta_1 - \zeta_2) + (P_1 + P_2)\nabla T\right] \ .
\end{aligned}$$

In the isotropic case the 3×3 matrices $\mathbf{D}_{ik} = d_{ik}\mathbf{I}$ are represented by scalar functions d_{ik}. In the symmetric isotropic case, in particular, we write

$$\mathbf{D} = \begin{pmatrix} d_1 & -\delta & f_1 \\ -\delta & d_2 & f_2 \\ f_1 & f_2 & d_u \end{pmatrix} \tag{5.4}$$

The positive definiteness of $\mathbf{D}_c$ becomes the condition $d_1 d_2 > \delta^2$. Moreover,

$$\mathbf{R} = \frac{1}{d_1 d_2 - \delta^2}(f_1 d_2 + f_2\delta\,,\ f_1\delta + f_2 d_1)\,\mathbf{I}$$

and $\mathbf{K} = \kappa\mathbf{I}$ with

$$\kappa = d_u - \frac{1}{d_1 d_2 - \delta^2}\left(f_1^2 d_2 + 2f_1 f_2\delta + f_2^2 d_1\right) > 0 \ .$$

The fluxes can be written in the familiar form

$$j_{n_i} = -\frac{d_i + \delta}{T}(-q_i\nabla\zeta_i + P_i\nabla T) + \frac{\delta}{T}\left[\nabla(\zeta_1 - \zeta_2) + (P_1 + P_2)\nabla T\right] \ .$$

Notice that the second summands of the carrier fluxes do not contribute anything to the electric current. In the case $\delta \equiv 0$ it is easy to identify $(d_i + \delta)/T$ with $n_i D_i$, where D_i denote the (scaled) mobilities or diffusion coefficients of the carriers. The case $\delta \neq 0$ has been introduced into simulation practice by D.E.Kane and R.M.Swanson [11] (or [12]), and the coefficients must be compared with their more specified formulas.

6 Several Temperatures

We want to include those hot electron effects which result, if the electrons do not instantaneously exchange energy with the lattice. Therefore we admit states $(\mathbf{n},\mathbf{T}) \equiv (n_0, n_1, n_2, T_0, T_1, T_2)$ in which the subsystems have its own temperatures, too. We shall see that there is a natural extension of the concepts, relations and arguments of the preceding sections to general states of partial local equilibrium. For the readers convenience we compile here some short notation which will be useful in this section, but we shall write often T instead of T_0.

$$
\begin{aligned}
\widetilde{\mathcal{P}}_i &\equiv M_i(T)T_i^{\alpha_i}\mathcal{F}_{\alpha_i} \circ \mathcal{F}^{-1}_{\alpha_i-1}\left[\frac{n_i}{M_i(T)T_i^{\alpha_i}}\right] \ , \\
\widetilde{\mathcal{Q}}_i &\equiv \frac{n_i^2}{M_i(T)T_i^{\alpha_i}\mathcal{F}_{\alpha_i-2} \circ \mathcal{F}^{-1}_{\alpha_i-1}\left[\frac{n_i}{M_i(T)T_i^{\alpha_i}}\right]} \ , \\
\widetilde{\mathcal{D}}_i &\equiv \widetilde{\mathcal{P}}_i - \widetilde{\mathcal{Q}}_i > -\frac{1}{\alpha_i}M_i(T)T_i^{\alpha_i}\mathcal{F}_{\alpha_i} \ , \\
a_i &\equiv \alpha_i\widetilde{\mathcal{P}}_i + \alpha_i^2\widetilde{\mathcal{D}}_i \ , \quad b_i \equiv \alpha_i L_i(T)\widetilde{\mathcal{D}}_i \ ,
\end{aligned}
$$

and

$$
a_0 \equiv c_L + T\sum_{j=0}^{2} q_j n_j E_j''(T) + \sum_{l=1}^{2}\left(\widetilde{\mathcal{P}}_l\,[TL_l(T)]' + L_l(T)^2\widetilde{\mathcal{D}}_l\right) \ .
$$

It is not difficult to guess those places in the expressions (3.1) or (3.2) where the (lattice) temperature T is to be substituted by the carrier temperatures T_i, if states of partial local equilibrium are considered, namely

$$
\begin{aligned}
\widetilde{s}_f(\mathbf{n},\mathbf{T}) = & c_L\log T + \sum_{j=0}^{2} q_j n_j E_j'(T) - \log\left[\left(\frac{n_0}{2(N_D-n_0)}\right)^{n_0}\left(\frac{N_D-n_0}{N_D}\right)^{N_D}\right] \\
& + \sum_{l=1}^{2}\left(\left[\alpha_l + 1 + L_l(T)\right]\widetilde{\mathcal{P}}_l - n_l\mathcal{F}^{-1}_{\alpha_l-1}\left[\frac{n_l}{M_l(T)T_l^{\alpha_l}}\right]\right)
\end{aligned}
\tag{6.1}
$$

and

$$
\widetilde{u}_f(\mathbf{n},\mathbf{T}) = c_L T - \sum_{j=0}^{2} q_j n_j[E_j(T) - TE_j'(T)] + \sum_{l=1}^{2}\left[\alpha_l T_l + TL_l(T)\right]\widetilde{\mathcal{P}}_l \ .
\tag{6.2}
$$

We shall see in Sect. 9 that this choice is confirmed by some general properties of the system. By admitting states with diverse temperatures, however, the state space has been extended in such a way that some thermodynamic concepts are not defined on the whole space or are no longer ’equivalent‘ as they are in states of partial local thermal equilibrium.

The abbreviations introduced above are justified by some useful formulas like

$$\begin{aligned} T_i\partial_{T_i}\widetilde{u}_f(\mathbf{n},\mathbf{T}) &= a_iT_i + b_iT \quad (i=1,2)\ , & T\partial_T\widetilde{u}_f(\mathbf{n},\mathbf{T}) &= a_0T + \textstyle\sum_{l=1}^2 b_lT_l\ , \\ T_i\partial_{T_i}\widetilde{s}_f(\mathbf{n},\mathbf{T}) &= a_i + b_i\ , \qquad \text{and} & T\partial_T\widetilde{s}_f(\mathbf{n},\mathbf{T}) &= a_0 + b_1 + b_2\ . \end{aligned}$$

Lemma 6.1 *The matrix*

$$\begin{pmatrix} a_1 & 0 & b_1 \\ 0 & a_2 & b_2 \\ b_1 & b_2 & a_0 \end{pmatrix} \tag{6.3}$$

is regular or even positively definite if and only if the inequality $\sum_{l=1}^2 b_l^2/a_l \neq a_0$ *or the estimate* $\sum_{l=1}^2 b_l^2/a_l < a_0$ *holds, respectively.*

*Proof.*As the inequalities

$$a_i = \alpha_i^2 M_i(T)T_i^{\alpha_i}\left[\left(\frac{1}{\alpha_i}+1\right)\mathcal{F}_{\alpha_i} - \frac{\mathcal{F}^2_{\alpha_i-1}}{\mathcal{F}_{\alpha_i-2}}\right] > 0 \qquad (i=1,2)$$

hold, the matrix (6.3) can be factorized,

$$\begin{pmatrix} \sqrt{a_1} & 0 & 0 \\ 0 & \sqrt{a_2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & b_1/\sqrt{a_1} \\ 0 & 1 & b_2/\sqrt{a_2} \\ b_1/\sqrt{a_1} & b_2/\sqrt{a_2} & a_0 \end{pmatrix} \begin{pmatrix} \sqrt{a_1} & 0 & 0 \\ 0 & \sqrt{a_2} & 0 \\ 0 & 0 & 1 \end{pmatrix} .$$

The central matrix is regular or positively definite if and only if the corresponding condition is fulfilled. □ Notice that

$$a_0 - \sum_{l=1}^{2}\frac{b_l^2}{a_l} \equiv c_L + T\partial_T^2\sum_{j=0}^{2} q_jn_jE_j(T) + \sum_{l=1}^{2}\widetilde{\mathcal{P}}_l\left([TL_l(T)]' + \frac{L_l(T)^2\widetilde{\mathcal{D}}_l}{\widetilde{\mathcal{P}}_l + \alpha_i\widetilde{\mathcal{D}}_l}\right) ,$$

and the condition $a_0 - \sum_{l=1}^2 b_l^2/a_l > 0$ is satisfied in the model case in which the band edges E_i and the coefficients M_i (i.e. the effective masses) do not depend on T. The inequality is checked in the Appendix for material laws which are used in simulation practice.

Proposition 6.1 *(Entropy maximum principle) If the matrix* (6.3) *is regular, the entropy maximum principle yields the equilibrium conditions* $T_1 = T_2 = T = 1/\lambda \equiv \theta$ *and*

$$\xi = -q_i \partial_{n_i} \left[\frac{1}{\theta} \widetilde{u}_f(\mathbf{n}, \theta, \theta, \theta) - \widetilde{s}_f(\mathbf{n}, \theta, \theta, \theta) \right] \quad = \quad - q_i \partial_{n_i} \left[\frac{1}{\theta} u_f(\mathbf{n}, \theta) - s_f(\mathbf{n}, \theta) \right] \ .$$

as in Prop. 3.1.

*Proof.*The proof is a straightforward application of the Lagrange method. The conditions for the thermal equilibrium are a system of three linear equations for three variables,

$$\begin{pmatrix} T_1 \partial_{T_1} \\ T_2 \partial_{T_2} \\ T \partial_T \end{pmatrix} [\widetilde{s}_f - \lambda \widetilde{u}_f] = \begin{pmatrix} a_1 & 0 & b_1 \\ 0 & a_2 & b_2 \\ b_1 & b_2 & a_0 \end{pmatrix} \begin{pmatrix} 1 - \lambda T_1 \\ 1 - \lambda T_2 \\ 1 - \lambda T \end{pmatrix} = 0 \ . \tag{6.4}$$

$\square$

Remark 6.1 *The derivatives of* E_i *and* M_i *with respect to* T *in the expressions* (6.1) *and* (6.2) *guarantee that the diverse temperatures coincide and are constant in the equilibrium states defined by the entropy maximum principle. If these terms had been omitted the diverse temperatures would neither coincide (with* $1/\lambda$*) nor be constant in equilibrium states.*

Remark 6.2 *For the states of partial local equilibrium electrochemical potentials* $\widetilde{\zeta}_i$ *are defined again according to the structure of the equilibrium densities. Thus the state equations*

$$n_0 = N_D \frac{2}{2 + \exp \frac{E_0(T) - \zeta_0}{T}}$$

and

$$n_i = M_i(T) T_i^{\alpha_i} \mathcal{F}_{\alpha_i - 1} \left[\frac{q_i}{T_i} \left(E_i(T) - \widetilde{\zeta}_i \right) \right] \qquad (i = 1, 2)$$

are a stringent consequence of the entropy maximum principle.

We introduce densities of energies of the subsystems,

$$\begin{aligned} u_i = u_f^{(i)}(n_i, T_i, T) \ &:= \ \alpha_i T_i \widetilde{\mathcal{P}}_i \qquad (i = 1, 2) \ , \quad \partial_{n_i} u_f^{(i)}(n_i, T_i, T) = \frac{\alpha_i}{n_i} T_i \widetilde{\mathcal{Q}}_i \ , \\ u_0 = u_f^{(0)}(\mathbf{n}, \mathbf{T}) \ &:= \ c_L T - \sum_{j=0}^{2} q_j n_j \left[E_j(T) - T E_j'(T) \right] + \sum_{l=1}^{2} T L_l(T) \widetilde{\mathcal{P}}_l \ . \end{aligned}$$

The following proposition is closely related to the entropy maximum principle.

Proposition 6.2 *If the matrix* (6.3) *is regular, the implicitly defined function*

$$\widetilde{s}\,(\mathbf{n},\mathbf{u}) := \widetilde{s}\left[\mathbf{n}, u_f^{(0)}, u_f^{(1)}, u_f^{(2)}\right] = \widetilde{s}_f\,(\mathbf{n},\mathbf{T})$$

is a thermodynamic potential. Its first-order partial derivatives are the conjugate variables

$$\partial_{u_0}\widetilde{s}\,(\mathbf{n},\mathbf{T}) = \frac{1}{T} \equiv \tau \ , \quad \partial_{u_i}\widetilde{s}\,(\mathbf{n},\mathbf{T}) = \frac{1}{T_i} \equiv \tau_i \ , \quad \partial_{n_0}\widetilde{s}\,(\mathbf{n},\mathbf{T}) = -\frac{\zeta_0}{T} \equiv -\xi_0 \equiv -\widetilde{\xi}_0 \ ,$$

and

$$\partial_{n_i}\widetilde{s}\,(\mathbf{n},\mathbf{T}) = q_i\left[\frac{\widetilde{\zeta}_i}{T_i} - E_i(T)\left(\frac{1}{T_i}-\frac{1}{T}\right)\right] \equiv q_i\widetilde{\xi}_i \qquad (i=1,2) \ .$$

The negative conjugate potential of $\widetilde{s}\,(\mathbf{n},\mathbf{u})$ *reads*

$$\begin{aligned}
&\widetilde{h}\left[\xi_0,\widetilde{\xi}_1,\widetilde{\xi}_2,\tau,\tau_1,\tau_2\right]\\
:=&\widetilde{s}_f\,[\mathbf{n},\mathbf{T}] - \frac{1}{T}\widetilde{u}_f\,[\mathbf{n},\mathbf{T}] - \sum_{l=1}^{2}\left(\frac{1}{T_l}-\frac{1}{T}\right)u_f^{(l)}(n_l,T_l,T) - \sum_{j=0}^{2} q_j n_j\widetilde{\xi}_j \\
=&c_L\,(\log T - 1) + N_D\Bigg\{\xi_0 - \frac{1}{T}E_0(T) + \log\Bigg[2+\exp\Bigg(\frac{1}{T}E_0(T)-\xi_0\Bigg)\Bigg]\Bigg] \\
&+\sum_{l=1}^{2} M_l(T)T_l^{\alpha_l}\mathcal{F}_{\alpha_l}\left[q_l\left(\frac{1}{T}E_l(T)-\widetilde{\xi}_l\right)\right]\Bigg\} \ .
\end{aligned}$$

Notice that the conjugate variables of n_1 and n_2 with respect to $\widetilde{s}$ on the state space of partial local equilibrium are extensions of the conjugate variables of n_1 and n_2 with respect to the restriction $\overline{s}$ of $\widetilde{s}$ onto the state space of partial local thermal equilibrium. The state variable ξ_0 will be considered as a fixed parameter again, and we shall stick to the variables T and T_i instead of the corresponding correct conjugate variables. Therefore we denote $\widetilde{h}\left(\xi_0,\widetilde{\xi}_1,\widetilde{\xi}_2,\tau,\tau_1,\tau_2\right) \equiv: \widetilde{H}\left(\widetilde{\xi}_1,\widetilde{\xi}_2,\mathbf{T}\right)$ and notice that $\partial_{\tau_i}\widetilde{h} \equiv -T_i^2\partial_{T_i}\widetilde{H}$ $(i=0,1,2)$. The first-order partial derivatives of $\widetilde{h}\,(\xi_0,\cdot,\cdot,\cdot,\cdot,\cdot,\cdot)$ are

$$\begin{aligned}
\partial_{\widetilde{\xi}_i}\widetilde{H}\left(\widetilde{\xi}_1,\widetilde{\xi}_2,\mathbf{T}\right) &= -q_iM_i(T)T_i^{\alpha_i}\mathcal{F}_{\alpha_i-1}\left[q_i\left(\frac{1}{T}E_i(T)-\widetilde{\xi}_i\right)\right] \quad (i=1,2) \ , \\
-T_i^2\partial_{T_i}\widetilde{H}\left(\widetilde{\xi}_1,\widetilde{\xi}_2,\mathbf{T}\right) &= -\alpha_iM_i(T)T_i^{\alpha_i+1}\mathcal{F}_{\alpha_i} \quad (i=1,2) \ ,
\end{aligned}$$

and

$$\begin{aligned}
-T^2\partial_T\widetilde{H}\left(\widetilde{\xi}_1,\widetilde{\xi}_2,\mathbf{T}\right) &= -c_LT - \left[E_0(T) - TE_0'(T)\right]N_D\frac{2}{2+\exp\left(\frac{1}{T}E_0(T)-\xi_0\right)} \\
&\quad+\sum_{l=1}^{2}\left\{q_l\left[E_l(T)-TE_l'(T)\right]M_l(T)T_l^{\alpha_l}\mathcal{F}_{\alpha_l-1} - TL_l(T)M_l(T)T_l^{\alpha_l}\mathcal{F}_{\alpha_l}\right\} \ .
\end{aligned}$$

The 5×5 matrix of second-order partial derivatives of the function $\widetilde{h}(\xi_0, \cdot, \cdot, \cdot, \cdot, \cdot)$ has a block matrix structure

$$\begin{pmatrix} \mathbf{A}_1 & 0 & F_1 \\ 0 & \mathbf{A}_2 & F_2 \\ F_1^T & F_2^T & A_0 \end{pmatrix}$$

with the positively definite symmetric matrices

$$\mathbf{A}_i = \begin{pmatrix} n_i \mathcal{F}_{\alpha_i - 2} / \mathcal{F}_{\alpha_i - 1} & q_i \alpha_i T_i n_i \\ q_i \alpha_i T_i n_i & \alpha_i(\alpha_i + 1) T_i^2 M_i(T) T_i^{\alpha_i} \mathcal{F}_{\alpha_i} \end{pmatrix} ,$$

with vectors

$$F_i = n_i \begin{pmatrix} q_i T L_i(T) - [E_i(T) - T E_i'(T)] \mathcal{F}_{\alpha_i - 2} / \mathcal{F}_{\alpha_i - 1} \\ \alpha_i T_i \left[(T L_i(T) \mathcal{F}_{\alpha_i} / \mathcal{F}_{\alpha_i - 1} - q_i [E_i(T) - T E_i'(T)] \right] \end{pmatrix} ,$$

and a diagonal element

$$\begin{aligned} A_0 = & c_L T^2 + T^3 \sum_{j=0}^{2} q_j n_j E_j'' + \frac{1}{N_D} [E_0(T) - T E_0'(T)]^2 n_0 \, (N_D - n_0) \\ & + \sum_{l=1}^{2} M_l(T) T_l^{\alpha_l} \left[T^2 \left([T L_l(T)]' + L_l(T)^2 \right) \mathcal{F}_{\alpha_l} \right. \\ & \left. -2 q_l T L_l(T) [E_l(T) - T E_l'(T)] \mathcal{F}_{\alpha_l - 1} + [E_l(T) - T E_l'(T)]^2 \mathcal{F}_{\alpha_l - 2} \right] . \end{aligned}$$

Lemma 6.2 *The matrix $d^2 \widetilde{h}(\xi_0, \ldots)$ is regular or even positively definite if and only if the inequality*

$$\sum_{l=1}^{2} F_l^T \mathbf{A}_l^{-1} F_l \neq A_0$$

or the estimate

$$\begin{aligned} A_0 - \sum_{l=1}^{2} F_l^T \mathbf{A}_l^{-1} F_l \equiv & \frac{1}{N_D} [E_0(T) - T E_0'(T)]^2 n_0 \, (N_D - n_0) + T^2 \left(a_0 - \sum_{l=1}^{2} \frac{b_l^2}{a_l} \right) \\ & - \sum_{l=1}^{2} n_l \alpha_l T^2 L_l(T)^2 \frac{\mathcal{F}_{\alpha_l} \mathcal{F}_{\alpha_l - 1}}{(\alpha_l + 1) \mathcal{F}_{\alpha_l} \mathcal{F}_{\alpha_l - 2} - \alpha_l \mathcal{F}_{\alpha_l - 1}^2} \\ & > 0 , \end{aligned}$$

respectively, holds.

*Proof.*The assertion becomes evidently by factorizing

$$\begin{pmatrix} \mathbf{A}_1^{1/2} & \mathbf{0} & 0 \\ \mathbf{0} & \mathbf{A}_2^{1/2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{I} & \mathbf{0} & \mathbf{A}_1^{-1/2} F_1 \\ \mathbf{0} & \mathbf{I} & \mathbf{A}_2^{-1/2} F_2 \\ F_1^T \mathbf{A}_1^{-1/2} & F_2^T \mathbf{A}_2^{-1/2} & A_0 \end{pmatrix} \begin{pmatrix} \mathbf{A}_1^{1/2} & \mathbf{0} & 0 \\ \mathbf{0} & \mathbf{A}_2^{1/2} & 0 \\ 0 & 0 & 1 \end{pmatrix} .$$

□

In the model case in which the band edges E_i and the coefficients M_i (i.e. the effective masses) do not depend on T the 5×5 matrix $d^2\widetilde{h}(\xi_0, \cdot, \cdot, \cdot, \cdot, \cdot)$ is positively definite. We consider it as an implicit assumption concerning the material laws E_i and M_i that the matrix is positively definite in general, too. The estimate is checked in the Appendix for material laws which are used in simulation practice. The function $\widetilde{h}(\xi_0, \cdot, \cdot, \cdot, \cdot, \cdot)$ is then strictly convex and has the partial derivatives

$$\partial_{\widetilde{\xi}_i}\widetilde{h} = -q_i n_i \ , \quad \partial_{T_i}\widetilde{h} = -u_f^{(i)} \quad (i = 1, 2) \ , \quad \text{and} \quad \partial_T \widetilde{h} = -u_f^{(0)} \ .$$

Remark 6.3 *The splitting $\widetilde{u}_f = \sum_{j=0}^{2} u_f^{(j)}$ is not arbitrary, but a consequence of the demand $\partial_{u_i}\widetilde{s} = \frac{1}{T_i}$ $(i = 1, 2)$ and $\partial_{u_0}\widetilde{s} = \frac{1}{T}$ (cf. Sect. 9).*

We are going to define thermodynamic forces that drive a homogeneous state of partial equilibrium into the corresponding equilibrium. There is no problem to substitute the reduced potentials ξ_1 or ξ_2 in the net reaction rates R_i by the quantities $\widetilde{\xi}_1$ or $\widetilde{\xi}_2$. Therefore, we choose the following extensions of the net reaction rates to the states of partial local equilibrium,

$$\widetilde{R}_0 = \widetilde{r}_0(\mathbf{n}, \mathbf{T}) \exp\left(\frac{1}{T_2}E_2(T) - \frac{1}{T_1}E_1(T)\right)\left[\exp\left(\widetilde{\xi}_1 - \widetilde{\xi}_2\right) - 1\right]$$

and

$$\widetilde{R}_i = \widetilde{r}_i(\mathbf{n}, \mathbf{T}) \exp\left(\frac{q_i}{T}E_0(T) - \frac{q_i}{T_{i^*}}E_{i^*}(T)\right)\left[\exp\left(q_i\widetilde{\xi}_{i^*} - q_i\xi_0\right) - 1\right] \ , \tag{6.5}$$

$(i = 1, 2;\ i^* = i - (-1)^i)$ with nonnegative material laws $\widetilde{r}_l$ $(l = 0, 1, 2)$, that are extensions of r_l.

We have seen that the system seemingly prefers the thermal equilibrium, i.e. the assimilation of the (reciprocal) temperatures, to the assimilation of the reduced potentials. Therefore the following system of differential equations describes the evolution of homogeneous states.

$$\begin{aligned}
\dot{n}_0 &= \widetilde{R}_2 - \widetilde{R}_1 \ , \\
\dot{n}_i &= -\widetilde{R}_0 - \widetilde{R}_{i^*} \qquad (i = 1, 2) \ ,
\end{aligned}$$

$$\begin{aligned}
\dot{T}_i \partial_{T_i} u_f^{(i)} + \dot{T} \partial_T u_f^{(i)} &= -q_i \lambda_0 \left(\frac{1}{T_1} - \frac{1}{T_2}\right) - \lambda_i \left(\frac{1}{T} - \frac{1}{T_i}\right) + \left(\widetilde{R}_0 + \widetilde{R}_{i^*}\right) \partial_{n_i} u_f^{(i)} \ , \\
\sum_{l=1}^{2} \dot{T}_l \partial_{T_l} u_f^{(0)} + \dot{T} \partial_T u_f^{(0)} &= \sum_{l=1}^{2} \left[\lambda_l \left(\frac{1}{T} - \frac{1}{T_l}\right) - \left(\widetilde{R}_0 + \widetilde{R}_{l^*}\right) \partial_{n_l} u_f^{(l)}\right] + \sum \widetilde{R}_\iota \widetilde{U}^\iota
\end{aligned}$$

with nonnegative material laws $\lambda_i = \lambda_i(\mathbf{n}, \mathbf{T})$ $(i = 0, 1, 2\ )$.

The same arguments as in Sect. 5 yield equations for the current densities of fluxes of particles or energies driven by the gradients of the conjugate variables. In the case of several temperatures the current equations read

$$\begin{pmatrix} \begin{pmatrix} \tilde{j}_{n_1} \\ \tilde{j}_{n_2} \end{pmatrix} \\ \begin{pmatrix} j_{u_1} \\ j_{u_2} \\ j_{u_0} \end{pmatrix} \end{pmatrix} = \begin{pmatrix} \mathbf{D} & \mathbf{B} \\ \mathbf{C} & \mathbf{Q} \end{pmatrix} \cdot \begin{pmatrix} \begin{pmatrix} -\nabla\tilde{\xi}_1 \\ \nabla\tilde{\xi}_2 \end{pmatrix} \\ \begin{pmatrix} \nabla\tau_1 \\ \nabla\tau_2 \\ \nabla\tau \end{pmatrix} \end{pmatrix} .$$

The requirement that the entropy production has to be positive implies again that the coefficient matrix and the block diagonal matrices has to be positive definite, in particular, regular matrices. Then we have

$$\begin{pmatrix} \begin{pmatrix} -\nabla\tilde{\xi}_1 \\ \nabla\tilde{\xi}_2 \end{pmatrix} \\ \begin{pmatrix} j_{u_1} \\ j_{u_2} \\ j_{u_0} \end{pmatrix} \end{pmatrix} = \begin{pmatrix} \mathbf{D}^{-1} & -\mathbf{D}^{-1}\mathbf{B} \\ \mathbf{C}\mathbf{D}^{-1} & \mathbf{Q} - \mathbf{C}\mathbf{D}^{-1}\mathbf{B} \end{pmatrix} \cdot \begin{pmatrix} \begin{pmatrix} \tilde{j}_{n_1} \\ \tilde{j}_{n_2} \end{pmatrix} \\ \begin{pmatrix} \nabla\tau_n \\ \nabla\tau_p \\ \nabla\tau \end{pmatrix} \end{pmatrix} .$$

The entropy production reads

$$\begin{aligned} \sigma = \begin{pmatrix} \tilde{j}_{n_1} & \tilde{j}_{n_2} \end{pmatrix} \cdot & \left[\mathbf{D}^{-1} \cdot \begin{pmatrix} \tilde{j}_{n_1} \\ \tilde{j}_{n_2} \end{pmatrix} - \mathbf{D}^{-1}\mathbf{B} \cdot \begin{pmatrix} \nabla\tau_1 \\ \nabla\tau_2 \\ \nabla\tau \end{pmatrix} \right] \\ + \begin{pmatrix} \nabla\tau_1 & \nabla\tau_2 & \nabla\tau \end{pmatrix} \cdot & \left[\mathbf{C}\mathbf{D}^{-1} \cdot \begin{pmatrix} \tilde{j}_{n_1} \\ \tilde{j}_{n_2} \end{pmatrix} + \mathbf{K} \cdot \begin{pmatrix} \nabla\tau_1 \\ \nabla\tau_2 \\ \nabla\tau \end{pmatrix} \right] \end{aligned}$$

with the heat conductivity matrix $\mathbf{K} = \mathbf{Q} - \mathbf{C}\mathbf{D}^{-1}\mathbf{B}$.

We consider the symmetric case $\mathbf{D} = \mathbf{D}^T$, $\mathbf{K} = \mathbf{K}^T$, and $\mathbf{C} = \mathbf{B}^T$. In this case the entropy production is diagonalized with respect to the block structure, i.e. the entropy production is the sum of the entropy production due to convectivity or electric conductivity and of the entropy production due to heat conductivity. The matrices $\mathbf{D}$ and $\mathbf{K}$ has to be positive definite in the symmetric case. We introduce the matrix $\widetilde{\mathbf{R}} := \mathbf{B}^T\mathbf{D}^{-1}$. The entropy flux

$$\begin{aligned}\widetilde{j}_s &= \begin{pmatrix} -\widetilde{\xi}_1 & \widetilde{\xi}_2 \end{pmatrix}\begin{pmatrix} \widetilde{j}_{n_1} \\ \widetilde{j}_{n_2} \end{pmatrix} + \begin{pmatrix} \tau_1 & \tau_2 & \tau \end{pmatrix}\begin{pmatrix} j_{u_1} \\ j_{u_2} \\ j_{u_0} \end{pmatrix} \\ &= \left[\begin{pmatrix} -\widetilde{\xi}_1 & \widetilde{\xi}_2 \end{pmatrix} + \begin{pmatrix} \tau_1 & \tau_2 & \tau \end{pmatrix}\widetilde{\mathbf{R}}\cdot\right]\begin{pmatrix} \widetilde{j}_{n_1} \\ \widetilde{j}_{n_2} \end{pmatrix} \\ &\quad + \begin{pmatrix} \tau_1 & \tau_2 & \tau \end{pmatrix}\mathbf{K}\cdot\begin{pmatrix} \nabla\tau_1 \\ \nabla\tau_2 \\ \nabla\tau \end{pmatrix}\end{aligned}$$

shows that the matrix $\widetilde{\mathbf{R}}$ is related to the entropies per carrier. A look onto the expression $\widetilde{s}_f$ shows that the entropies per carrier read

$$\widetilde{P}_i = [\alpha_i + 1 + L_i(T)]\,\frac{\mathcal{F}_{\alpha_i}}{\mathcal{F}_{\alpha_i - 1}} + q_i\left[\widetilde{\xi}_i + \frac{1}{T}\left(E_i(T) - TE_i'(T)\right)\right]$$

$(i = 1, 2)$. Writing the entropy flux with the matrix $\widetilde{\mathbf{R}}$ we see that the relations

$$\widetilde{P}_i - q_i\widetilde{\xi}_i = \sum_{j=1}^{2}\frac{\widetilde{R}_{ij}}{T_j} + \frac{\widetilde{R}_{i0}}{T} \qquad (i = 1, 2)$$

hold. These formulas suggest the identity

$$\widetilde{\mathbf{R}} = \begin{pmatrix} [\alpha_1 + 1 + L_1(T)]\,\frac{\mathcal{F}_{\alpha_1}}{\mathcal{F}_{\alpha_1 - 1}} & 0 \\ 0 & [\alpha_2 + 1 + L_2(T)]\,\frac{\mathcal{F}_{\alpha_2}}{\mathcal{F}_{\alpha_2 - 1}} \\ E_1(T) - TE_1'(T) & -[E_2(T) - TE_2'(T)] \end{pmatrix}.$$

The carrier fluxes are

$$\begin{pmatrix} \widetilde{j}_{n_1} \\ \widetilde{j}_{n_2} \end{pmatrix} = \mathbf{D}\cdot\begin{pmatrix} \mathbf{x}_1 \\ \mathbf{x}_2 \end{pmatrix}$$

with the thermodynamic forces

$$\begin{aligned}\mathbf{x}_i =& q_i\nabla\widetilde{\xi}_i + [\alpha_i + 1 + L_i(T)]\,\frac{\mathcal{F}_{\alpha_i}}{\mathcal{F}_{\alpha_i - 1}}\nabla\tau_i - q_i[E_i(T) - TE_i'(T)]\nabla\tau \\ =& \frac{q_i}{T_i}\nabla\widetilde{\zeta}_i - \frac{1}{T_i}\left(q_i\widetilde{\zeta}_i + [\alpha_i + 1 + L_i(T)]\,\frac{\mathcal{F}_{\alpha_i}}{\mathcal{F}_{\alpha_i - 1}}\right)\nabla\log T_i + \frac{q_i}{T}[E_i(T) - TE_i'(T)]\nabla\log T\end{aligned}$$

i.e. $\mathbf{x}_n$, $\mathbf{x}_p$, $\nabla\tau_n$, $\nabla\tau_p$, and $\nabla\tau$ is a basis in the space of thermodynamic forces which diagonalizes the entropy production with respect to the block matrix structure,

$$\sigma = \begin{pmatrix} \mathbf{x}_n & \mathbf{x}_p \end{pmatrix}\cdot\left[\mathbf{D}\cdot\begin{pmatrix} \mathbf{x}_n \\ \mathbf{x}_p \end{pmatrix}\right] + \begin{pmatrix} \nabla\tau_n & \nabla\tau_p & \nabla\tau \end{pmatrix}\cdot\left[\mathbf{K}\cdot\begin{pmatrix} \nabla\tau_n \\ \nabla\tau_p \\ \nabla\tau \end{pmatrix}\right].$$

The following theorem is the summary of the preceding discussion.

Theorem 6.1 *The density of entropy* $s = \widetilde{s}_f[\mathbf{n}, \mathbf{T}]$ *of any solution of the system of evolution equations*

$$\begin{aligned}
\dot{n}_0 &= \widetilde{R}_2 - \widetilde{R}_1 \ , \\
\dot{n}_i + \nabla \cdot \widetilde{j}_{n_i} &= -\widetilde{R}_0 - \widetilde{R}_{i*} \qquad (i = 1, 2) \ ,
\end{aligned} \tag{6.6}$$

$$\begin{aligned}
\dot{T}_i \partial_{T_i} u_f^{(i)} + \dot{T} \partial_T u_f^{(i)} + \nabla \cdot j_{u_i} &= -\lambda_0 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) - \lambda_i \left(\frac{1}{T} - \frac{1}{T_i} \right) \\
&\quad + \left(\widetilde{R}_0 + \widetilde{R}_{i*} + \nabla \cdot \widetilde{j}_{n_i} \right) \partial_{n_i} u_f^{(i)} \qquad (i = 1, 2) \ , \\
\sum_{l=1}^{2} \dot{T}_l \partial_{T_l} u_f^{(0)} + \dot{T} \partial_T u_f^{(0)} + \nabla \cdot j_{u_0} &= \sum_{l=1}^{2} \lambda_l \left(\frac{1}{T} - \frac{1}{T_l} \right) + \sum \widetilde{R}_\iota \widetilde{U}^\iota \\
&\quad + \textstyle\sum_{l=1}^{2} \left[(\nabla \cdot \widetilde{j}_{n_l}) \partial_{n_l} u_f^{(0)} - \left(\widetilde{R}_0 + \widetilde{R}_{l*} \right) \partial_{n_l} u_f^{(l)} \right]
\end{aligned} \tag{6.7}$$

satisfies the entropy balance equation

$$\begin{aligned}
\dot{s} + \nabla \cdot j_s = \lambda_0 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^2 &+ \sum_{l=1}^{2} \lambda_l \left(\frac{1}{T} - \frac{1}{T_l} \right)^2 \\
&+ (\widetilde{\xi}_1 - \widetilde{\xi}_2) \widetilde{R}_0 + \left(\xi_0 - \widetilde{\xi}_2 \right) \widetilde{R}_1 + \left(\widetilde{\xi}_1 - \xi_0 \right) \widetilde{R}_2 \\
&+ \begin{pmatrix} \begin{pmatrix} -\nabla \widetilde{\xi}_1 \\ \nabla \widetilde{\xi}_2 \end{pmatrix} \\ \begin{pmatrix} \nabla \frac{1}{T_1} \\ \nabla \frac{1}{T_2} \\ \nabla \frac{1}{T} \end{pmatrix} \end{pmatrix} \cdot \left[\begin{pmatrix} \mathbf{D} & \mathbf{B} \\ \mathbf{B}^T & \mathbf{Q} \end{pmatrix} \cdot \begin{pmatrix} \begin{pmatrix} -\nabla \widetilde{\xi}_1 \\ \nabla \widetilde{\xi}_2 \end{pmatrix} \\ \begin{pmatrix} \nabla \frac{1}{T_1} \\ \nabla \frac{1}{T_2} \\ \nabla \frac{1}{T} \end{pmatrix} \end{pmatrix} \right]
\end{aligned} \tag{6.8}$$

with the entropy flux

$$j_s = \sum_{l=1}^{2} q_l \widetilde{\xi}_l \widetilde{j}_{n_l} + \sum_{k=0}^{2} \frac{1}{T_k} j_{u_k} \ . \tag{6.9}$$

*Proof.*A consequence of Prop. 6.2 is the identity

$$\left(\ \partial_{T_1} \widetilde{s}_f \quad \partial_{T_2} \widetilde{s}_f \quad \partial_T \widetilde{s}_f\ \right) \begin{pmatrix} \partial_{T_1} u_f^{(1)} & 0 & \partial_T u_f^{(1)} \\ 0 & \partial_{T_2} u_f^{(2)} & \partial_T u_f^{(2)} \\ \partial_{T_1} u_f^{(0)} & \partial_{T_2} u_f^{(0)} & \partial_T u_f^{(0)} \end{pmatrix}^{-1} = \left(\ \tfrac{1}{T_1} \quad \tfrac{1}{T_2} \quad \tfrac{1}{T}\ \right) , \tag{6.10}$$

but the identity

$$\left(\ \partial_{T_1} \widetilde{s}_f \quad \partial_{T_2} \widetilde{s}_f \quad \partial_T \widetilde{s}_f\ \right) = \left(\ \tfrac{1}{T_1} \quad \tfrac{1}{T_2} \quad \tfrac{1}{T}\ \right) \begin{pmatrix} \partial_{T_1} u_f^{(1)} & 0 & \partial_T u_f^{(1)} \\ 0 & \partial_{T_2} u_f^{(2)} & \partial_T u_f^{(2)} \\ \partial_{T_1} u_f^{(0)} & \partial_{T_2} u_f^{(0)} & \partial_T u_f^{(0)} \end{pmatrix}$$

holds also for a singular matrix (6.3). Taking regard to this identity and applying the evolution equations one obtains

$$\begin{aligned}
\dot{s} =& \sum_{j=0}^{2} \left[\dot{T}_j \partial_{T_j} \widetilde{s}_f + \dot{n}_j \partial_{n_j} \widetilde{s}_f \right] \\
\\
=& \lambda_0 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^2 + \sum_{l=1}^{2} \lambda_l \left(\frac{1}{T} - \frac{1}{T_l} \right)^2 - \sum_{k=0}^{2} \frac{1}{T_k} \nabla \cdot j_{u_k} - \sum_{l=1}^{2} q_l \widetilde{\xi}_l \nabla \cdot \widetilde{j}_{n_l} \\
& \sum_{\iota=0}^{2} \widetilde{R}_\iota \left(\frac{1}{T} \widetilde{U}^\iota - \widetilde{S}^\iota \right) + \sum_{l=1}^{2} \left(\frac{1}{T_l} - \frac{1}{T} \right) \left(\widetilde{R}_0 + \widetilde{R}_{l^*} \right) \partial_{n_l} u_f^{(l)} \\
\\
=& \lambda_0 \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^2 + \sum_{l=1}^{2} \lambda_l \left(\frac{1}{T} - \frac{1}{T_l} \right)^2 - \sum_{k=0}^{2} \frac{1}{T_k} \nabla \cdot j_{u_k} - \sum_{l=1}^{2} q_l \widetilde{\xi}_l \nabla \cdot \widetilde{j}_{n_l} \\
& + \widetilde{R}_0 \sum_{l=1}^{2} \partial_{n_l} \left[\frac{1}{T} u_f^{(0)} - \widetilde{s}_f + \frac{1}{T_l} u_f^{(l)} \right] \\
& + \sum_{l=1}^{2} \widetilde{R}_l \left[\partial_{n_{l^*}} \left(\frac{1}{T} u_f^{(0)} - \widetilde{s}_f + \frac{1}{T_{l^*}} u_f^{(l^*)} \right) - q_l \partial_{n_0} \left(\frac{1}{T} \widetilde{u}_f - \widetilde{s}_f \right) \right] \quad .
\end{aligned}$$

The divergence terms provide the divergence of the entropy current density and the part of the entropy production rate due to the current densities. From the identities

$$\begin{aligned}
& \partial_{n_l} \left[\frac{1}{T} u_f^{(0)} - \widetilde{s}_f + \frac{1}{T_l} u_f^{(l)} \right] = \partial_{n_l} \left[\frac{1}{T} \widetilde{u}_f - \widetilde{s}_f + \left(\frac{1}{T_l} - \frac{1}{T} \right) u_f^{(l)} \right] \\
&= \partial_{n_l} \left\{ -\frac{q_l}{T} n_l E_l(T) + n_l \mathcal{F}_{\alpha_l - 1}^{-1} - M_l(T) T_l^{\alpha_l} \mathcal{F}_{\alpha_l} \circ \mathcal{F}_{\alpha_l - 1}^{-1} \right\} \\
&\quad = -q_l \left[\frac{\widetilde{\zeta}_l}{T_l} - \left(\frac{1}{T_l} - \frac{1}{T} \right) E_l(T) \right] = -q_l \widetilde{\xi}_l
\end{aligned}$$

and $\partial_{n_0} \left(\frac{1}{T} \widetilde{u}_f - \widetilde{s}_f \right) \equiv \partial_{n_0} \left(\frac{1}{T} u_f - s_f \right) = \xi_0$ (cf. (3.3) with $i = 0$) we get the positively definite expression

$$\begin{aligned}
& \widetilde{R}_0 \sum_{l=1}^{2} \partial_{n_l} \left[\frac{1}{T} u_f^{(0)} - \widetilde{s}_f + \frac{1}{T_l} u_f^{(l)} \right] \\
& + \sum_{l=1}^{2} \widetilde{R}_l \left[\partial_{n_{l^*}} \left(\frac{1}{T} u_f^{(0)} - \widetilde{s}_f + \frac{1}{T_{l^*}} u_f^{(l^*)} \right) - q_l \partial_{n_0} \left(\frac{1}{T} \widetilde{u}_f - \widetilde{s}_f \right) \right] \\
=& \widetilde{R}_0 \left(\widetilde{\xi}_1 - \widetilde{\xi}_2 \right) + \sum_{l=1}^{2} \widetilde{R}_l \left(q_l \widetilde{\xi}_{l^*} - q_l \xi_0 \right) \quad .
\end{aligned}$$

□

Remark 6.4 *The positive definiteness of the entropy production rate remains preserved if the thermodynamic forces* $\frac{1}{T} - \frac{1}{T_i}$ *or* $\frac{1}{T_1} - \frac{1}{T_2}$ *are substituted by arbitrary expressions* $X_i\left(\frac{1}{T}, \frac{1}{T_i}\right)$ *or* $X_0\left(\frac{1}{T_1}, \frac{1}{T_2}\right)$ *with the property* $X_l(x,y)\,(x-y) > 0$ $(x \neq y)$.

7 Electrostatic Interaction

In this section we complete the energy model by including the electrostatic interaction which is described by the electrostatic potential Ψ on the domain Ω. This potential is defined as the solution $\Psi \equiv: \mathbf{P}^{\omega}_{\Gamma_D}(N_D - n_0 - n_1 + n_2)$ of a boundary value problem $\Pi^{\omega}_{\Gamma_D}(N_D - n_0 - n_1 + n_2)$ for the Poisson equation

$$-\nabla \cdot (\varepsilon \nabla \Psi) = d + N_D - n_0 - n_1 + n_2 \ .$$

We discuss three boundary conditions, namely the homogeneous Neumann condition ($\omega \equiv 0$ and $\Gamma_D = \emptyset$), the boundary condition of the third kind,

$$\varepsilon \partial_\nu \Psi + \omega \Psi = \omega g$$

on the whole boundary $\partial\Omega$ with a given nonnegative function $\omega \neq 0$ and boundary values g ($\Gamma_D = \emptyset$ and not $\omega \equiv 0$), and the mixed boundary condition, $\Psi = \psi^D$ on some proper subset $\Gamma_D \subset \partial\Omega$ of the boundary and the boundary condition of the third kind on the complementary set $\Gamma = \partial\Omega \setminus \Gamma_D$. The homogeneous Neumann condition has only model character; it is particularly compatible with thermodynamically closed systems. The boundary condition of the third kind connects in some sense the homogeneous Neumann condition ($\omega \equiv 0$) with the Dirichlet condition $\Psi = g$ (ω very large); it is, moreover, the favoured boundary condition on the gate contacts of the semiconductor device. The mixed boundary condition, finally, satisfies the needs of device simulation in the best way. The boundary value problems are formulated as integral identities. Let $H_\emptyset \equiv H^1(\Omega)$ denote the space of square integrable functions which have square integrable derivatives (in the sense of the theory of distributions) of first order. The homogeneous Neumann problem $\Pi^0_\emptyset(N_D - n_0 - n_1 + n_2)$ asks for potentials $\Psi \in H_\emptyset$ which satisfy the integral identity

$$\int \varepsilon \nabla \psi \cdot \nabla \chi \, d\Omega = \int \chi (d + N_D - n_0 - n_1 + n_2)\, d\Omega \qquad (\chi \in H_\emptyset) \ .$$

The problem has a solution only in the case that the global charge neutrality condition $\int (d + N_D - n_0 - n_1 + n_2)\, d\Omega = 0$ is fulfilled; the solution is determined up to an arbitrary additive constant, but there is just one solution $\mathbf{P}^0_\emptyset(N_D - n_0 - n_1 + n_2)$ which satisfies the orthogonality condition $\int \Psi \, d\Omega = 0$. The integral formulation of the second boundary value problem reads

$$\int \varepsilon \nabla \Psi \cdot \nabla \chi \, d\Omega + \int_{\partial\Omega} \omega \Psi \chi \, d\Gamma = \int \chi (d + N_D - n_0 - n_1 + n_2)\, d\Omega + \int_{\partial\Omega} \omega g \chi \, d\Gamma$$

$(\chi \in H_{\emptyset})$. In the case of mixed boundary condition let $H_{\Gamma_D} \equiv H_0^1(\Omega \cup \Gamma)$ denote the space of those functions $\chi \in H^1(\Omega)$ which vanish on the portion Γ_D of the boundary. The integral formulation of the mixed boundary value problem reads again

$$\int \varepsilon \nabla \Psi \cdot \nabla \chi \, d\Omega + \int_\Gamma \omega \Psi \chi \, d\Gamma = \int \chi (d + N_D - n_0 - n_1 + n_2) \, d\Omega + \int_\Gamma \omega g \chi \, d\Gamma$$

$(\chi \in H_{\Gamma_D})$.

We may assume that ψ^D does not only represent the Dirichlet data on the portion Γ_D of the boundary, but that it represents the external electric field, $\psi^D \equiv \mathbf{P}^\omega_{\Gamma_D}(0)$, meanwhile $\psi := \Psi - \psi^D$ represents the internal electric field. There are a Green kernel $G^\omega_{\Gamma_D}$ on $\Omega \times \Omega$ and a Poisson kernels $P^\omega_{\Gamma_D}$ on $\Omega \times \Gamma_D$ and Q^ω_Γ on $\Omega \times \Gamma$ such that

$$\psi^D = \int_\Omega G^\omega_{\Gamma_D}(\cdot, y) d(y) \, dy + \int_{\Gamma_D} P^\omega_{\Gamma_D} \psi^D(\cdot, z) \psi^D(z) \, d\Gamma(z) + \int_\Gamma Q^\omega_{\Gamma_D}(\cdot, z) g(z) \, d\Gamma(z) \; .$$

If the boundary data $f = \psi^D | \Gamma_D$ or g depend on the time t, then ψ^D depends also on time and its derivative with respect to time reads

$$\dot{\psi}^D = \int_{\Gamma_D} P^\omega_{\Gamma_D} \psi^D(\cdot, z) \dot{f}(z,t) \, d\Gamma(z) + \int_\Gamma Q^\omega_{\Gamma_D}(\cdot, z) \dot{g}(z,t) \, d\Gamma(z) \; .$$

We associate an electrostatic energy $U^\omega_{\Gamma_D}(\rho)$ $(\rho \equiv N_D - n_0 - n_1 + n_2)$ with each boundary value problem, namely

$$U^0_{\emptyset}(\rho) = \frac{1}{2} \int \varepsilon \left| \nabla \Psi \right|^2 \, d\Omega$$

and

$$\begin{aligned} U^\omega_{\Gamma_D}(\rho) &= \frac{1}{2} \int \varepsilon \left| \nabla \psi^D \right|^2 \, d\Omega + \frac{1}{2} \int_\Gamma \omega \left| \psi^D \right|^2 \, d\Gamma + \int \rho \psi^D \, d\Omega \\ &+ \frac{1}{2} \int \varepsilon \left| \nabla \psi \right|^2 \, d\Omega + \frac{1}{2} \int_\Gamma \omega \left| \psi \right|^2 \, d\Gamma \end{aligned}$$

in the case $\omega \neq 0$ or $\Gamma_D \neq \emptyset$.

Lemma 7.1 *Both energies are chosen in a plausible way and satisfy*

$$\langle dU^\omega_{\Gamma_D}(\rho), \delta\rho \rangle = \int \Psi \delta\rho \, d\Omega$$

for arbitrary variations $\delta\rho$ *which has to satisfy* $\int \delta\rho \, d\Omega = 0$ *in the case* $\omega = 0$ *and* $\Gamma_D = \emptyset$.

*Proof.*Indeed, the solution $\delta\psi$ of the Poisson equation for $\delta\rho$ under homogeneous boundary conditions satisfies either

$$\begin{aligned} U^0_{\emptyset}(\rho+\delta\rho) &= \frac{1}{2}\int \varepsilon \left|\nabla(\Psi+\delta\psi)\right|^2 \, d\Omega \\ &= U^0_{\emptyset}(\rho) + \int \varepsilon \nabla\Psi \cdot \nabla\delta\psi \, d\Omega + \frac{1}{2}\int \varepsilon \left|\nabla\delta\psi\right|^2 \, d\Omega \\ &= U^0_{\emptyset}(\rho) + \int \Psi\delta\rho \, d\Omega + \frac{1}{2}\int \varepsilon \left|\nabla\delta\psi\right|^2 \, d\Omega \end{aligned}$$

or

$$\begin{aligned} U^\omega_{\Gamma_D}(\rho+\delta\rho) &= U^\omega_{\Gamma_D}(0) + \int (\rho+\delta\rho)\psi^D \, d\Omega \\ &\quad + \frac{1}{2}\int \varepsilon \left|\nabla(\psi+\delta\psi)\right|^2 \, d\Omega + \frac{1}{2}\int_\Gamma \omega \left|\psi+\delta\psi\right|^2 \, d\Gamma \\ &= U^\omega_{\Gamma_D}(\rho) + \int \delta\rho\psi^D \, d\Omega + \int \varepsilon\nabla\psi \cdot \nabla\delta\psi \, d\Omega + \int_\Gamma \omega\psi\delta\psi \, d\Gamma \\ &\quad + \frac{1}{2}\int \varepsilon \left|\nabla\delta\psi\right|^2 \, d\Omega + \frac{1}{2}\int_\Gamma \omega|\delta\psi|^2 \, d\Gamma \\ &= U^\omega_{\Gamma_D}(\rho) + \int \delta\rho\Psi \, d\Omega + \frac{1}{2}\int \varepsilon \left|\nabla\delta\psi\right|^2 \, d\Omega + \frac{1}{2}\int_\Gamma \omega|\delta\psi|^2 \, d\Gamma \ , \end{aligned}$$

i.e. the assertion. □

In the case of local thermal equilibrium we introduce the free energy by

$$\mathcal{F}(\mathbf{n},T) := U^\omega_{\Gamma_D}(N_D - n_0 - n_1 + n_2) + \int f[\mathbf{n},T] \, d\Omega \ .$$

This functional satisfies evidently

$$\langle \partial_T \mathcal{F}(\mathbf{n},T), \delta T\rangle = \int \delta T \partial_T f[\mathbf{n},T] \, d\Omega = -\int s_f[\mathbf{n},T]\delta T \, d\Omega \ .$$

We define

$$\begin{aligned} \mathcal{U}_f(\mathbf{n},T) &:= \mathcal{F}(\mathbf{n},T) + \int s_f[\mathbf{n},T]T \, d\Omega \\ &= U^\omega_{\Gamma_D}(N_D - n_0 - n_1 + n_2) + \int u_f[\mathbf{n},T] \, d\Omega \end{aligned}$$

and

$$\widetilde{\mathcal{U}}_f(\mathbf{n},\mathbf{T}) := U^\omega_{\Gamma_D}(N_D - n_0 - n_1 + n_2) + \int \widetilde{u}_f[\mathbf{n},\mathbf{T}] \, d\Omega \ .$$

Proposition 7.1 *(Entropy maximum principle) The entropy*

$$\widetilde{\mathcal{S}}_f(\mathbf{n},\mathbf{T}) := \int \widetilde{s}_f[\mathbf{n},\mathbf{T}]\, d\Omega$$

realizes its constrained maximum under the constraints

$$U_0 = \widetilde{\mathcal{U}}_f(\mathbf{n},\mathbf{T}) \quad \textit{and} \quad Q_0 = \int (N_D - n_0 - n_1 + n_2)\, d\Omega$$

($Q_0 = -\int d\, d\Omega$ if $\omega = 0$ and $\Gamma_D = \emptyset$) at one of the equilibrium states which are characterized by the equilibrium conditions of coinciding constant temperature θ and coinciding constant reduced potentials ξ, $T_1 \equiv T_2 \equiv T = 1/\lambda = \theta$ and

$$\xi = q_i \partial_{n_i} \left[\widetilde{\mathcal{S}}_f(\mathbf{n},\theta,\theta,\theta) - \frac{1}{\theta} \widetilde{\mathcal{U}}_f(\mathbf{n},\theta,\theta,\theta) \right] \qquad (i = 0,1,2)\ .$$

The equilibrium densities are

$$\overline{n}_0[\xi,\theta,\overline{\Psi}(\xi,\theta)] = N_D \frac{2}{2 + \exp\left[\frac{1}{\theta}\left(E_0(\theta) - \overline{\Psi}(\xi,\theta)\right) - \xi\right]}$$

and

$$\overline{n}_i[\xi,\theta,\overline{\Psi}(\xi,\theta)] = M_i(\theta)\theta^{\alpha_i} \mathcal{F}_{\alpha_i - 1}\left[-q_i \left(\xi + \frac{\overline{\Psi}(\xi,\theta) - E_i(\theta)}{\theta} \right) \right] \qquad (i = 1,2)\ .$$

The equilibrium potential $\overline{\Psi}(\xi,\theta)$ is the solution of the nonlinear Poisson equation

$$\Psi = \mathbf{P}^{\omega}_{\Gamma_D} \left[N_D + \sum_{j=0}^{2} q_j \overline{n}_j(\xi,\theta) \right]\ .$$

*Proof.*The proof is again a straightforward application of the Lagrange method. Indeed

$$0 = \langle \partial_{T_i} \left[\widetilde{\mathcal{S}}_f - \lambda \widetilde{\mathcal{U}}_f \right],\, \delta T \rangle = \int \delta T\, \partial_{T_i} \left[\widetilde{s}_f - \lambda \widetilde{u}_f \right]\, d\Omega \qquad (i = 0,1,2)$$

for arbitrary variations δT yield the system (6.4) and thus $T_1 \equiv T_2 \equiv T = 1/\lambda = \theta$. The other conditions are

$$\begin{aligned} 0 &= \langle \partial_{n_i} \left(\widetilde{\mathcal{S}}_f[\mathbf{n},\theta,\theta,\theta] - \frac{1}{\theta} \widetilde{\mathcal{U}}_f[\mathbf{n},\theta,\theta,\theta] \right), \delta n \rangle - q_i \int \xi \delta n\, d\Omega \\ &= \int \delta n \left[\partial_{n_i} \left(\widetilde{s}_f[\mathbf{n},\theta,\theta,\theta] - \frac{1}{\theta} \widetilde{u}_f[\mathbf{n},\theta,\theta,\theta] \right) - q_i \xi \right]\, d\Omega \end{aligned}$$

$(i = 0, 1, 2)$ for arbitrary variations δn, i.e. the assertion. □

The values (ξ, θ) of the equilibrium defined by the parameters Q_0 and U_0 in the constraints are the solution of a system of two highly nonlinear equations which arises if the equilibrium densities and $\theta = T_1 = T_2 = T$ are put in the constraints. The electrochemical potentials ζ_i are defined now by the state equations

$$n_0 = N_D \frac{2}{2 + \exp \frac{E_0(T) - \Psi - \zeta_0}{T}} \, , \tag{7.1}$$

and

$$n_i = M_i(T) T_i^{\alpha_i} \mathcal{F}_{\alpha_i - 1} \left[-q_i \frac{1}{T_i} \left(\zeta_i + \Psi - E_i(T) \right) \right] \qquad (i = 1, 2) \, , \tag{7.2}$$

(7.3)

where Ψ is the solution of the nonlinear Poisson equation

$$\Psi = \mathbf{P}^{\omega}_{\Gamma_D} \left\{ N_D \left[1 - \frac{2}{2 + \exp \frac{E_0(T) - \Psi - \zeta_0}{T}} \right] \right. \\ \left. + \sum_{l=1}^{2} q_l M_l(T) T_l^{\alpha_l} \mathcal{F}_{\alpha_l - 1} \left[-q_l \frac{1}{T_l} \left(\zeta_l + \Psi - E_l(T) \right) \right] \right\} \, .$$

Notice that the electrochemical potentials appear here as independent state variables, but the densities as dependent ones, and that the state equations reflect the principle of partial local equilibrium.

Remark 7.1 *The equations are not so deterent as they seem to be. They are, in particular, uniquely solvable by comfortable methods because of monotony properties of associated operators.*

According to (3.3) or Prop. 6.2 the conjugate variables of the densities with respect to the entropy considered as a thermodynamic potential are closely related to the entropy maximum principle combined with the principle of partial local equilibrium. These relations hold also for the corresponding systems with the electrostatic interaction, i.e. the relations

$$\xi_i = q_i \partial_{n_i} s_f[\mathbf{n}, T] - \frac{q_i}{T} \left(\partial_{n_i} u_f[\mathbf{n}, T] - \Psi \right) = \frac{\zeta_i}{T} \quad (i = 0, 1, 2) \, , \tag{7.4}$$

and

$$\begin{aligned}
\widetilde{\xi}_i &= q_i\partial_{n_i} s_f[\mathbf{n},\mathbf{T}] - \frac{q_i}{T_i}\left(\partial_{n_i} u_f^{(i)} - \Psi\right) - \frac{q_i}{T}\partial_{n_i} u_f^{(0)} \\
&\equiv q_i\partial_{n_i}\left(\widetilde{s}_f - \sum_{l=1}^{2}\frac{1}{T_i}u_f^{(i)} - \frac{1}{T}u_f^{(0)}\right) + \frac{q_i}{T_i}\Psi \\
&= \frac{\widetilde{\zeta}_i}{T_i} - E_i(T)\left(\frac{1}{T_i} - \frac{1}{T}\right) , \qquad (7.5)
\end{aligned}$$

respectively, hold for the systems with electrostatic interaction.

Theorem 7.1 *Let* $(\mathbf{n},\mathbf{T})$ *be any solution of the system of evolution equations*

$$\begin{aligned}
\dot{n}_0 &= \widetilde{R}_2 - \widetilde{R}_1 , \\
\dot{n}_i + \nabla\cdot\widetilde{j}_{n_i} &= -\widetilde{R}_0 - \widetilde{R}_{i*} \qquad (i=1,2) , \qquad (7.6)
\end{aligned}$$

$$\begin{aligned}
\dot{T}_i\partial_{T_i}u_f^{(i)} + \dot{T}\partial_T u_f^{(i)} + \nabla\cdot j_{u_i} &= -q_i\lambda_0\left(\frac{1}{T_1} - \frac{1}{T_2}\right) - \lambda_i\left(\frac{1}{T} - \frac{1}{T_i}\right) \\
&\quad + \left(\widetilde{R}_0 + \widetilde{R}_{i*} + \nabla\cdot\widetilde{j}_{n_i}\right)\left[\partial_{n_i}u_f^{(i)} - \Psi\right] \qquad (i=1,2) , \\
\sum_{l=1}^{2}\dot{T}_l\partial_{T_l}u_f^{(0)} + \dot{T}\partial_T u_f^{(0)} + \nabla\cdot j_{u_0} &= \sum_{l=1}^{2}\lambda_l\left(\frac{1}{T} - \frac{1}{T_l}\right) + \left(\widetilde{R}_1 - \widetilde{R}_2\right)\left(\partial_{n_0}\widetilde{u}_f - \Psi\right) \\
&\quad + \sum_{l=1}^{2}\left(\widetilde{R}_0 + \widetilde{R}_{l*} + \nabla\cdot\widetilde{j}_{n_l}\right)\partial_{n_l}u_f^{(0)}
\end{aligned}$$

with the electrostatic potential $\Psi = \mathbf{P}^{\omega}_{\Gamma_D}(N_D - n_0 - n_1 + n_2)$*. The density of total energy of this solution,*

$$\widetilde{u} = \frac{\varepsilon}{2}\left|\nabla\Psi\right|^2 + \widetilde{u}_f(\mathbf{n},\mathbf{T}) \qquad (7.7)$$

and its flux

$$\widetilde{j}_{\widetilde{u}} = \sum_{l=0}^{2} j_{u_l} - \Psi\varepsilon\nabla\dot{\Psi} = \widetilde{j}_u - \Psi\varepsilon\nabla\dot{\Psi} \qquad (7.8)$$

satisfy the conservation law

$$\partial_t[\widetilde{u}] + \nabla\cdot\widetilde{j}_{\widetilde{u}} = 0 \ .$$

The corresponding density of entropy satisfies the entropy balance equation (6.8)*.*

*Proof.*On the one hand the identity

$$\begin{aligned}\partial_t[\widetilde{u}] + \nabla \cdot \widetilde{j}_{\tilde{u}} &= \varepsilon \nabla\Psi \cdot \nabla\dot{\Psi} - \nabla \cdot \left(\Psi \varepsilon \nabla \dot{\Psi}\right) + \partial_t[\widetilde{u}_f] + \nabla \cdot \sum_{l=0}^{2} j_{u_l} \\ &= -\Psi \nabla \cdot \left(\varepsilon \nabla \dot{\Psi}\right) + \partial_t[\widetilde{u}_f] + \nabla \cdot \widetilde{j}_u \\ &= \Psi \sum_{l=0}^{2} q_l \dot{n}_l + \partial_t[\widetilde{u}_f] + \nabla \cdot \widetilde{j}_u\end{aligned}$$

holds, where the Poisson equation differentiated with respect to the time has been applied. On the other hand the sum of the three energy balance equations reads

$$\begin{aligned}&\sum_{l=0}^{2} \dot{T}_l \partial_{T_l} \widetilde{u}_f + \nabla \cdot \widetilde{j}_u \\ &= -\sum_{l=0}^{2} \dot{n}_l \partial_{n_l} \widetilde{u}_f + \Psi \sum_{l=1}^{2} \left(\widetilde{R}_0 + \widetilde{R}_{l*} + \nabla \cdot \widetilde{j}_{n_l} + q_l \widetilde{R}_l\right) \ ,\end{aligned}$$

i.e. $\partial_t[\widetilde{u}] + \nabla \cdot \widetilde{j}_{\tilde{u}} = 0$.

The entropy density $s = \widetilde{s}_f[\mathbf{n}, \mathbf{T}]$ of a solution of (7.6) satisfies

$$\begin{aligned}\dot{s} \equiv& \sum_{l=0}^{2} \left[\dot{T}_l \partial_{T_l} \widetilde{s}_f + \dot{n}_l \partial_{n_l} \widetilde{s}_f\right] \\ =& \sum_{l=1}^{2} \frac{q_l}{T_l} \left[-\lambda_0 \left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \lambda_l \left(\frac{1}{T} - \frac{1}{T_l}\right) + \nabla \cdot j_{u_l}\right] \\ &+ \sum_{l=1}^{2} \left(R_0 + R_{l*} + \nabla \cdot \widetilde{j}_{n_l}\right) \left[\frac{1}{T_l} \left(\partial_{n_l} u_f^{(l)} - \Psi\right) + \frac{1}{T} \partial_{n_l} u_f^{(0)} - \partial_{n_l} \widetilde{s}_f\right] \\ &+ \frac{1}{T} \left[\sum_{l=1}^{2} \lambda_l \left(\frac{1}{T} - \frac{1}{T_l}\right) - \nabla \cdot j_{u_0}\right] + \left(\widetilde{R}_1 - \widetilde{R}_2\right) \left[\frac{1}{T} \left(\partial_{n_0} \widetilde{u}_f - \Psi\right) - \partial_{n_0} \widetilde{s}_f\right] \\ =& \lambda_0 \left(\frac{1}{T_1} - \frac{1}{T_2}\right)^2 + \sum_{l=1}^{2} \lambda_l \left(\frac{1}{T} - \frac{1}{T_l}\right)^2 - \sum_{l=0}^{2} \frac{1}{T_l} \nabla \cdot j_{u_l} \\ &- \sum_{l=1}^{2} \widetilde{\xi}_l \left(\widetilde{R}_0 + \widetilde{R}_{l*} + \nabla \cdot \widetilde{j}_{n_l}\right) + \xi_0 \left(\widetilde{R}_1 - \widetilde{R}_2\right)\end{aligned}$$

because of (6.10), (7.6), and (7.5). The divergence terms provide the divergence of the entropy current density and the part of the entropy production rate due to the current densities. □

Remark 7.2 *The conservation law of energy would also allow to omit the terms* $\widetilde{R}_\iota \Psi$ *in the energy balance equations for the subsystems, but the entropy balance equation does not tolerate this change!*

The following theorem is proved analogously.

Theorem 7.2 *Let* $(\mathbf{n}, T)$ *be a solution of the following system of evolution equations*

$$\begin{aligned} \dot{n}_0 &= R_2 - R_1 \ , \\ \dot{n}_i + \nabla \cdot j_{n_i} &= -R_0 - R_{i^*} \qquad (i = 1, 2) \ , \\ \dot{T} \partial_T u_f + \nabla \cdot j_u &= \sum_{\iota=0}^{2} R_\iota U^\iota + \sum_{l=1}^{2} (\partial_{n_l} u_f - \Psi) \nabla \cdot j_{n_l} \end{aligned} \tag{7.9}$$

with the electrostatic potential $\Psi = \mathbf{P}^\omega_{\Gamma_D}(N_D - n_0 - n_1 + n_2)$. *The density of total energy of this solution,*

$$\overline{u} = \frac{\varepsilon}{2} |\nabla \Psi|^2 + u_f(\mathbf{n}, T)$$

and its flux

$$j_{\overline{u}} = j_u - \Psi \varepsilon \nabla \dot{\Psi}$$

satisfy the conservation law

$$\partial_t [\overline{u}] + \nabla \cdot j_{\overline{u}} = 0 \ .$$

The density of entropy $s = s_f[\mathbf{n}, T]$ *satisfies the entropy balance equation* (5.2) *with the entropy flux* (5.3).

Remark 7.3 *The relations* (7.5) *or* (7.4) *guarantee the generally expected behaviour of the entropy density* $s = \widetilde{s}_f$ *or* $s = s_f$ *of solutions of either the system* (7.6) *or the system* (7.9) *of evolution equations. As these systems has been based on rather elementary principles only, we intend to accept them as the correct formulation of energy models.*

Remark 7.4 *Notice that the densities* $\widetilde{u}$ *or* $\overline{u}$ *coincide with the densities of* $\widetilde{\mathcal{U}}_f$ *or* $\mathcal{U}_f$ *only in the case that the electrostatic potential satisfies the homogeneous Neumann condition. The reason is that in general the electrostatic energy cannot be restricted to the domain* Ω *in the 'real electrostatic world', and our choice is a necessary compromise and approximation.*

Remark 7.5 *In a certain sense, the system* (7.6) *is an extension of the system* (7.9). *It should be noticed, however, that the temperatures* $T_i(t)$ *of a solution of* (7.6) *with coinciding initial temperatures* $T_1(0) = T_2(0) = T(0)$ *need not and will not coincide for later times* $t > 0$. *A-posteriori experience may show, nevertheless, that in a class of situations it is not necessary to solve the more expensive system* (7.6), *because the differences* $T_i(t) - T(t)$ *are negligible.*

In the discussion after a lecture on the subject in the Langenbach seminar Prof. K. Gröger suggested to regard the conjugacy of the variables more consequently in the evolution equations. Indeed, the system (7.9) can be written more lucidly

$$\begin{aligned} \dot{n}_0 &= \overline{R}_2 - \overline{R}_1 \ , \\ \dot{n}_i + \nabla \cdot \overline{j}_{n_i} &= -\overline{R}_0 - \overline{R}_{i^*} \qquad (i = 1, 2) \ , \\ \dot{u} + \nabla \cdot \overline{j}_u &= \Psi \nabla \cdot \left(\overline{j}_{n_2} - \overline{j}_{n_1} \right) \end{aligned}$$

with kinetic or transport coefficients

$$\overline{r}_0(\mathbf{n}, u) \equiv r_0(\mathbf{n}, T) \exp\left(\frac{1}{T} \left[E_2(T) - E_1(T) \right] \right)$$

etc, and the system (7.6) can be written

$$\begin{aligned} \dot{n}_0 &= \hat{R}_2 - \hat{R}_1 \ , \\ \dot{n}_i + \nabla \cdot \hat{j}_{n_i} &= -\hat{R}_0 - \hat{R}_{i^*} \qquad (i = 1, 2) \ , \\ \dot{u}_i + \nabla \cdot \hat{j}_{u_i} &= -q_i \hat{\lambda}_0 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) - \hat{\lambda}_i \left(\frac{1}{T} - \frac{1}{T_i} \right) \\ &\quad - \left(\hat{R}_0 + \hat{R}_{i^*} + \nabla \cdot \hat{j}_{n_i} \right) \Psi (i = 1, 2) \ , \\ \dot{u}_0 + \nabla \cdot \hat{j}_{u_0} &= \sum_l \hat{\lambda}_l \left(\frac{1}{T} - \frac{1}{T_l} \right) - \left(\hat{R}_1 - \hat{R}_2 \right) \Psi \end{aligned} \tag{7.10}$$

with kinetic or transport coefficients $\hat{\lambda}_i (\mathbf{n}, \mathbf{u}) \equiv \lambda_i (\mathbf{n}, \mathbf{T})$ etc. It might be more natural or more convenient, at least in principle, to evaluate primarily the independent variables $\mathbf{n}$, and u or $\mathbf{u}$ from these systems of evolution equations, but evaluate secondarily temperatures by means of either the nonlinear equation $u_f(\mathbf{n}, T) = u$ or the system of nonlinear equations

$$\begin{aligned} u_f^{(i)}(n_i, T_i, T) &= u_i \qquad (i = 1, 2) \ , \\ u_f(\mathbf{n}, \mathbf{T}) - \sum_{l=1}^{2} u_f^{(l)}(n_l, T_l, T) &= u_0 \ . \end{aligned}$$

It must be said, however, that these densities are conjugate to the state variables ξ_i and $1/T$ or to the state variables $\widetilde{\xi}_i$ and $1/T_j$ only in a generalized sense, because we do not know a thermodynamic potential 'entropy' in these cases. It seems to be more usual, moreover, to describe material laws in dependence upon the temperature(s) than in dependence upon the energy or the energies.

8 The case of Boltzmann statistics

If the Boltzmann statistics can be applied to the carriers in the conduction band and in the valence band, the formulas become much simpler. In this case $\widetilde{\mathcal{P}}_i \equiv \widetilde{\mathcal{Q}}_i$

reduces to n_i $(i = 1, 2)$, i.e. $a_i = \alpha_i n_i$ and $b_i = 0$. and the densities of entropy and energy read

$$\begin{aligned} \widetilde{s}_f^B &= c_L \log T + \sum_{j=0}^{2} q_j n_j E_j'(T) - \log \left[\left(\frac{n_0}{2(N_D - n_0)} \right)^{n_0} \left(\frac{N_D - n_0}{N_D} \right)^{N_D} \right] \\ &\quad + \sum_{l=1}^{2} n_l \left[\alpha_l + 1 + L_l(T) - \log \frac{n_l}{M_l(T) T_l^{\alpha^l}} \right] \ , \\ \widetilde{u}_f^B &= c_L T - \sum_{j=0}^{2} q_j n_j \left[E_j(T) - T E_j'(T) \right] + \sum_{l=1}^{2} n_l \left[\alpha_l T_l + T L_l(T) \right] \ , \end{aligned}$$

and $u_f^{(i)} = \alpha_i T_i n_i$ $(i = 1, 2)$. The conditions for the thermal equilibrium (cf. (6.4) with $b_i = 0$) are three decoupled linear equations, i.e. the subsystems are weaker coupled in the Boltzmann case than in the Fermi-Dirac statistics. This observation is also confirmed by the formulas

$$T_i \partial_{T_i} \widetilde{s}_f^B = \partial_{T_i} \widetilde{u}_f^B = \partial_{T_i} u_f^{(i)} \quad \text{and} \quad T \partial_T \widetilde{s}_f^B = \partial_T \widetilde{u}_f^B = \partial_T u_f^{(0)} \ .$$

The coefficients r_ι or $\widetilde{r}_\iota$ $(\iota = 0, 1, 2\ )$, $\overline{\mathbf{D}}$, D_1, D_2, δ or λ_j $(j = 0, 1, 2)$ may be different in the two statistics, but the structure of the net recombination rates and of the fluxes remain unchanged. The nonlinear Poisson equation changes, too, but the qualitative properties, which base on the monotony properties of associated operators, remain unchanged.

We consider only states of partial local thermal equilibrium and the case of symmetric isotropic current equations. The complete system of evolution equations reads in the case of Boltzmann statistics

$$\begin{aligned} (8.1) \qquad \dot{n}_0 &= R_2 - R_1 \ , \\ \dot{n}_i + \nabla \cdot j_{n_i} &= -R_0 - R_{i^*} \qquad (i = 1, 2) \ , \\ \dot{T} \partial_T u_f^B + \nabla \cdot j_u &= \sum_{\iota=0}^{2} R_\iota U^\iota + \sum_{l=1}^{2} \left[T \left(\alpha_l + L_l(T) \right) + q_l \left(\Psi - E_l(T) + T E_l'(T) \right) \right] \nabla \cdot j_{n_l} \end{aligned}$$

with the electrostatic potential $\Psi = \mathbf{P}^{\omega}_{\Gamma_D}(p + N_D - N - n)$, with the density of internal energy

(8.2)

$$u_f^B(\mathbf{n}, T) = c_L T - \sum_{j=0}^{2} q_j n_j \left[E_j(T) - T E_j'(T) \right] + T \sum_{l=1}^{2} n_l \left[\alpha_l + L_l(T) \right] \ ,$$

with the current densities

(8.3)

$$j_{n_i} = -n_i D_i \left(-q_i \nabla \zeta_i + P_i \nabla T\right) + \frac{\delta}{T} \left[\nabla \left(\zeta_1 - \zeta_2\right) + \left(P_1 + P_2\right) \nabla T\right] \ ,$$

(8.4)

$$j_u = \sum_{l=1}^{2} \left(T P_l - q_l \zeta_l\right) j_{n_l} - \frac{\kappa}{T^2} \nabla T \ ,$$

(8.5)

$$P_i = \alpha_i + 1 + L_i(T) - \log \frac{n_i}{M_i(T) T^{\alpha_i}} = \alpha_i + 1 + L_i(T) + \frac{q_i}{T} \left[\zeta_i + \Psi - E_i(T)\right] \ ,$$

with the net reaction rates

(8.6)

$$R_0 = r_0(\mathbf{n}, T) \exp\left(\frac{1}{T}\left[E_2(T) - E_1(T)\right]\right) \left[\exp\left(\frac{1}{T}\left[\zeta_1 - \zeta_2\right]\right) - 1\right]$$

and

$$R_i = r_i(\mathbf{n}, T) \exp\left(-\frac{q_i}{T}\left[E_{i^*}(T) - E_0(T)\right]\right) \left[\exp\left(\frac{q_i}{T}\left[\zeta_{i^*} - \zeta_0\right]\right) - 1\right] \qquad (i = 1, 2)$$

$(i^* = i - (-1)^i)$ and with

$$U^0 = -\sum_{l=1}^{2} q_l \left[E_l(T) - T E_l'(T) + T L_l(T)\right]$$

and

$$U^i = q_i \left[\left[E_{i^*}(T) - T E_{i^*}'(T) + T L_{i^*}(T) - E_0(T) + T E_0'(T)\right] \qquad (i = 1, 2) \ .$$

9 Miscellanous topics.

In Sect. 6 we have guessed state equations for the densities of internal energy $\widetilde{u}_f$ and of entropy $\widetilde{s}_f$ of a model of a semiconductor device with carrier temperatures (hot electrons). These densities generalize the densities u_f and s_f, which are derived from the density f of a free energy in the usual way, from states of partial local thermal equilibrium to states of partial local equilibrium with specified carrier temperatures T_1 and T_2. In this section we shall discuss related topics more systematically. To this aim it will be enough to consider a reduced system with electrons only. The mentioned densities of energy and of entropy for such a simplified model read

$$\widetilde{u}_f(n, T_n, T) = c_L T + n\left[E(T) - T E'(T)\right] + T_n \left[\alpha + L(T)\right] \widetilde{\mathcal{P}}$$

and

$$\widetilde{s}_f(n,T_n,T) = c_L \log T - nE'(T) - n\mathcal{F}_{\alpha-1}^{-1}\left[\frac{n}{M(T)T_n^{\alpha}}\right] + \left[1+\alpha+\frac{T_n}{T}\right]\widetilde{\mathcal{P}}$$

with the abbreviations $L(T) := T\,[\log M(T)]'$ and

$$\widetilde{\mathcal{P}} := M(T)T_n^{\alpha}\mathcal{F}_{\alpha} \circ \mathcal{F}_{\alpha-1}^{-1}\left[\frac{n}{M(T)T_n^{\alpha}}\right] \ .$$

We have seen that

- the entropy maximum principle applied to these expressions yields the usual states of equilibrium,
- the principle of partial local equilibrium yields the state equation

  $$n = M(T)T_n^{\alpha}\mathcal{F}_{\alpha-1}\left[\frac{1}{T_n}[\widetilde{\zeta} - E(T)]\right] \ ,$$

  which can be considered as the definition of the (electro)chemical potential $\widetilde{\zeta}$ or the reduced potential $\widetilde{\zeta}/T_n$ of electrons,
- the function $u_f^n(n,T_n,T) \equiv \alpha T_n \widetilde{\mathcal{P}}$ can be considered as the density u_n of energy of the subsystem of electrons,
- the implicitly defined function

  $$\widetilde{s}\left[n, u_f^n(n,T_n,T), \widetilde{u}_f(n,T_n,T) - u_f^n(n,T_n,T)\right] = \widetilde{s}_f(n,T_n,T)$$

  has the properties of a thermodynamical potential that respects the decomposition of the system into two subsystems, namely,
- the conjugate variables of u_n, $u_L \equiv \widetilde{u}_f - u_f^n$, and n are $\frac{1}{T_n} = \partial_{u_n}\widetilde{s}\left[n, u_f^n, \widetilde{u}_f - u_f^n\right]$, $\frac{1}{T} = \partial_{u_L} s\left[n, u_f^n, \widetilde{u}_f - u_f^n\right]$, and $\widetilde{\xi} := \frac{\widetilde{\zeta}}{T_n} - E(T)\left(\frac{1}{T_n} - \frac{1}{T}\right)$.

Although in systems of irreversible thermodynamics the energy and the entropy can exchange their role to some extent, we shall see that there is no function $s_n = s_f^n$ in general such that an implicitly defined function

$$\widetilde{u}\left[n, s_f^n(n,T_n,T), \widetilde{s}_f(n,T_n,T) - s_f^n(n,T_n,T)\right] = \widetilde{u}_f(n,T_n,T)$$

would satisfy the analogous relations $\partial_{s_n}\widetilde{u}\left[n, s_f^n, \widetilde{s}_f - s_f^n\right] = T_n$ and $\partial_{s_L}\widetilde{u}\left[n, s_f^n, \widetilde{s}_f - s_f^n\right] = T$. Indeed, these requirements would imply the differential relations

$$\begin{aligned}(T_n - T)\partial_{T_n} s_f^n = \partial_{T_n}\widetilde{u}_f - T\partial_{T_n}\widetilde{s}_f \; &= \; \frac{1}{T_n}(aT_n + bT) - \frac{T}{T_n}(a+b) \; = \; (T_n - T)\frac{a}{T_n} \\ &= (T_n - T)\frac{\alpha}{T_n}\left[(\alpha+1)\widetilde{\mathcal{P}} - \alpha\widetilde{\mathcal{Q}}\right]\end{aligned}$$

and

$$\begin{aligned}(T_n - T)\partial_T s_f^n = \partial_T\widetilde{u}_f - T\partial_T\widetilde{s}_f \; &= \; \frac{1}{T}(a_T^0 T + bT_n) - a_T^0 - b \; = \; (T_n - T)\frac{b}{T} \\ &= (T_n - T)\frac{L(T)}{T}\alpha\left[\widetilde{\mathcal{P}} - \widetilde{\mathcal{Q}}\right]\end{aligned}$$

with the abbreviation

$$\widetilde{\mathcal{Q}} \equiv \frac{n^2}{M(T)T_n^\alpha \mathcal{F}_{\alpha-2} \circ \mathcal{F}_{\alpha-1}^{-1}\left[\frac{n}{M(T)T_n^\alpha}\right]} ,$$

but the integrability condition $\partial_T\left[\partial_{T_n} s_f^n\right] \equiv \partial_{T_n}\left[\partial_T s_f^n\right]$ is violated in general, for

$$\partial_T\left[\partial_{T_n} s_f^n\right] - \partial_{T_n}\left[\partial_T s_f^n\right] \equiv \frac{\alpha}{T_n}\frac{L(T)}{T}\left[\widetilde{\mathcal{P}} - \widetilde{\mathcal{Q}}\right] .$$

With regard to systems with electrostatic interaction such a splitting of entropy would be useful, however, because in the case of local thermal equilibrium the total energy

$$\mathcal{U}\left[n, s_f\right] \equiv \int u_f[n, T]\, d\Omega + U_{\Gamma_D}^{\omega}(-n)$$

has the properties of the thermodynamic potential, namely,

$$\langle \partial_T\left[\mathcal{U}\left(n, s_f[n, T]\right)\right] \, , \, \delta T\rangle = \int \delta T\,\partial_T u_f[n, T]\, d\Omega \; = \; \int \delta T\, T\,\partial_T s_f[n, T]\, d\Omega \; ,$$

i.e.

$$\langle \partial_s\mathcal{U}\left(n, s\right) \, , \, \delta s\rangle = \int T\delta s\, d\Omega \; ,$$

and

$$\langle \partial_n\left[\mathcal{U}\left(n, \widetilde{s}_f[n, T_n, T]\right)\right] \, , \, \delta n\rangle = \int \delta n\left[\partial_n u_f - T s_f - \Psi\right]\, d\Omega = \int \delta n\,\zeta\, d\Omega \; .$$

In contrast to that definition, there are some problems to find a functional space for the total energy such that $\mathcal{S}[n,u] \equiv \int s_f[n,T]\,d\Omega$ can be understood analogously, i.e. $\langle \partial_u \mathcal{S}\,(n,u)\ ,\ \delta u\rangle = \langle \frac{1}{T}, \delta u\rangle$ etc. It seems that the functional space of the total energy should be a dual space of a space of functions on the domain Ω which contains the reciprocal temperature.

We return to systems without electrostatic interaction and ask for other choises of densities of energy and entropy instead of $\widetilde{u}_f$ and $\widetilde{s}_f$. We start with densities

$$\hat{s}_f(n,T_n,T) :\equiv -\partial_{T_n}\hat{f}(n,T_n,T) - \partial_T \hat{f}(n,T_n,T)$$

and

$$\hat{u}_f(n,T_n,T) :\equiv \hat{f}(n,T_n,T) - T_n\partial_{T_n}\hat{f}(n,T_n,T) - T\partial_T\hat{f}(n,T_n,T)$$

associated with a function $\hat{f}(n,T_n,T)$. In the case of local thermal equilibrium $T_n \equiv T$ the functions $f(n,T) \equiv \hat{f}(n,T,T)$, $s_f(n,T) \equiv \hat{s}_f(n,T,T)$, and $u_f(n,T) \equiv \hat{u}_f(n,T,T)$ are the densities of free energy and the corresponding entropy and energy. We apply the entropy maximum principle. The Lagrange method yields the equilibrium conditions

$$\begin{aligned} 0 &= \partial_{T_n}\left[\hat{s}_f - \lambda\hat{u}_f\right] = -(1-\lambda T_n)\partial^2_{T_n}\hat{u}_f(n,T_n,T) - (1-\lambda T)\partial_{T_n}\partial_T\hat{f}(n,T_n,T)\ , \\ 0 &= \partial_T\left[\hat{s}_f - \lambda\hat{u}_f\right] = -(1-\lambda T_n)\partial_{T_n}\partial_T\hat{f}(n,T_n,T) - (1-\lambda T)\partial^2_T\hat{f}(n,T_n,T)\ , \end{aligned}$$

and

$$\xi = \lambda\partial_n\hat{u}_f - \partial_n\hat{s}_f\ .$$

If the matrix $d^2\hat{f}(n,\cdot,\cdot)$ of the second order partial derivatives with respect to the temperatures is regular, the first two equations define the states of thermal equilibrium $T_n \equiv T \equiv 1/\lambda \equiv: \theta$. Under these conditions the third equation becomes $\xi = \frac{1}{\theta}\partial_n\hat{f}(n,\theta,\theta)$. The principle of partial local equilibrium reads in this case $\zeta \equiv \partial_n\hat{f}(n,T_n,T)$ and yields the corresponding state equation, which means nothing else than the definition of the (electro)chemical potential ζ of electrons.

We check now the possibility of splitting the energy $\hat{u}_f = u^n_f + (\hat{u}_f - u^n_f)$ or the entropy $\hat{s}_f = s^n_f + (\hat{s}_f - s^n_f)$ in this general setting. We look for a function s^n_f such that the implicitly defined function $\hat{u}\left[n, s^n_f, \hat{s}_f - s^n_f\right] = \hat{u}_f$ has the properties of a thermodynamic potential which respects the decomposition of the system into two subsystems, namely, which satisfies the identities $\partial_{s_n}\hat{u} = \theta$ and $\partial_{s_L}\hat{u} = T$. These requirements are the identities

$$(T_n - T)\partial_{T_n}s^n_f = -(T_n - T)\partial^2_{T_n}\hat{f}(n,T_n,T)$$

and

$$(T_n - T)\partial_T s_f^n = -(T_n - T)\partial_T \partial_{T_n} \hat{f}(n, T_n, T) \ ,$$

which are trivially satisfied by the function $s_f^n = -\partial_{T_n} \hat{f}$. The conjugate variable of n with respect to the potential $\hat{u}(n, s_n, s_L)$ becomes

$$\partial_n \hat{u} = \partial_n \hat{u}_f - T\partial_n \hat{s}_f - (T_n - T)\partial_n s_f^n = \partial_n \hat{f} \ .$$

Remark 9.1 *A consequence of this observation is that the densities* $\widetilde{u}_f(\mathbf{n}, \mathbf{T})$ *and* $\widetilde{s}_f(\mathbf{n}, \mathbf{T})$ *can not be derived from a free energy* $\widetilde{f}(\mathbf{n}, \mathbf{T})$ *in general!*

The question for a function u_f^n with the property that the implicitly defined entropy $\hat{s}(n, u_f^n, \hat{u}_f - u_f^n) = \hat{s}_f$ has the properties of a thermodynamic potential which respects the decomposition of the system into two subsystems yields analogously the differential identities $\partial_{T_n} u_f^n = -T_n \partial_{T_n}^2 \hat{f}$ and $\partial_T u_f^n = -T_n \partial_T \partial_{T_n} \hat{f}$. The ansatz

$$u_f^n(n, T_n, T) = \hat{f}(n, T_n, T) - T_n \partial_{T_n} \hat{f}(n, T_n, T) + g(n, T)$$

with an arbitrary function g which does not depend on T_n satisfies the first identity and is even its general solution. The second identity yields the differential equation

$$\partial_T \hat{f} - T_n \partial_T \partial_{T_n} \hat{f} + \partial_T g = -T_n \partial_T \partial_{T_n} \hat{f} \ ,$$

i.e. $\hat{f}(n, T_n, T) = g(n, T) + h(n, T_n)$. The result has a plausible interpretation, namely, the energy of the whole system is the sum of the energies of the two subsystems only if also the free energy of the whole system is the sum of the free energies of the two subsystems and if the free energy of each subsystem does not depend on the temperature of the other subsystem. The associated state equation reads $\zeta = \partial_n g(n, T) + \partial_n h(n, T_n)$, but such state equations are not realistic ones in semiconductor models with carrier temperatures.

10 Discussion

To compare the equations of the proposed energy model (7.9) with those of other authors we write the fourth equation of (7.9) as a heat equation with $C \equiv \partial_T u_f$, i.e. we start from the equation

$$C\dot{T} - \nabla \cdot j_u = \sum_{\iota=0}^{2} R_\iota U^\iota + \sum_{l=1}^{2} (\partial_{n_l} u_f + q_l \Psi) \nabla \cdot j_{n_l} \ .$$

In the discussion we shall restrict ourselves to the case of Boltzmann statistics and we shall neglect the contribution of the trap level, i.e.

$$C\dot{T} - \nabla \cdot j_u = \sum_{l=1}^{2} \left[T\alpha_l + TL_l(T) + q_l[\Psi - E_l(T) + TE_l'(T)]\right](R_0 + \nabla \cdot j_{n_l}) \ .$$

Specifying the energy current density and neglecting the electron-hole scattering effect ($\delta = 0$) we get

$$C\dot{T} - \nabla \cdot \left[\frac{\kappa}{T^2}\nabla T\right] = H$$

with a heat generation term

$$\begin{aligned} H = & \sum_{l=1}^{2} \left[T\alpha_l + TL_l(T) + q_l[\Psi - E_l(T) + TE_l'(T)]\right](R_0 + \nabla \cdot j_{n_l}) \\ & - \nabla \cdot \sum_{l=1}^{2} (TP_l - q_l\zeta_l)\, j_{n_l} \\ = & \sum_{l=1}^{2} \left[T\alpha_l + TL_l(T) + q_l[\Psi - E_l(T) + TE_l'(T)]\right](R_0 + \nabla \cdot j_{n_l}) \\ & + \sum_{l=1}^{2} \left[\frac{1}{n_l D_l}\left|j_{n_l}\right|^2 - T\nabla \cdot (P_l j_{n_l})\, q_l\zeta_l\nabla \cdot j_{n_l}\right] \\ = & \sum_{l=1}^{2} \left[\frac{1}{n_l D_l}\left|j_{n_l}\right|^2 - T\nabla \cdot (P_l j_{n_l}) + TR_0\,(\alpha_l + L_l(T))\right] + R_0\left[E_g(T) - TE_g'(T)\right] \\ & + \sum_{l=1}^{2} (\nabla \cdot j_{n_l})\left[T\alpha_l + TL_l(T) + q_l\left(\zeta_l + \Psi - E_l(T) + TE_l'(T)\right)\right] \ . \end{aligned}$$

Notice that in the case of Boltzmann statists

$$\zeta_i = E_i(T) - \Psi - q_i T \log \frac{n_i}{M_i(T)T^{\alpha_i}} \equiv \zeta_{i\,f}(n_1, n_2, T)$$

and thus for a completely ionized doping profile the identity

$$\zeta_i - T\partial_T\zeta_{i\,f} = \alpha_i T + TL_i(T) + q_i[\Psi - E_i(T) + TE_i'(T)]$$

holds. Therefore the heat source term is just Wachutka's heat source term

$$H = \sum_{l=1}^{2} \left[\frac{1}{n_l D_l}\left|j_{n_l}\right|^2 - T\nabla \cdot (P_l j_{n_l}) - q_l R_0\,(\zeta_l - T\partial_T\zeta_{l\,f}) + q_l T\partial_T\zeta_{l\,f}\nabla \cdot j_{n_l}\right]$$

(cf. [20],(29)).

Some authors (cf. [15], [17], [7]) prefer other versions of the energy balance equation than we propose in this preprint. They prefer the point of view that the system is a system of carriers in an external field Ψ. Diverse versions of energy and energy fluxes are considered and adapted entropies are applied. Notice that in expressions for the densities of energy or entropy which are obtained immediatly from carrier distribution functions no terms appear which contain derivatives of the band edges or of the effective masses with respect to the temperature. J.E. Parrott balanced the energy density $U := u_f + E_2 n_2 - E_1 n_1$ for a system without traps (cf. [17], (20a)) with the energy current density $u :\equiv j_u + \sum_{l=1}^{2} q_l (E_l - \Psi) j_{n_l}$. Since this balance equation is equivalent to the heat flow equation, it is as acceptable as our energy balance equation.

P. Degond et al. [7] describe a very simple energy-transport model for semiconductors in a more general setting. The system (7.10) specified to their simple example reads

$$\begin{array}{rcl} \dot{n} + \nabla \cdot j_n &=& 0\,,\\ \dot{u}_n + \nabla \cdot j_{u_n} &=& -\lambda \left(\frac{1}{T} - \frac{1}{T_n}\right) - \Psi \nabla \cdot j_n \end{array} \quad \text{with} \quad \begin{pmatrix} j_n \\ j_{u_n} \end{pmatrix} = \mathbf{D} \begin{pmatrix} -\nabla \frac{\zeta}{T_n} \\ \nabla \frac{1}{T_n} \end{pmatrix}$$

with symmetric positively definite 2 × 2 matrix. Therefore $u_n \equiv U$ and $j_{u_n} = I_2$ in their notation, i.e. they consider the energy balance equation in two versions, either

$$\dot{u}_n + \nabla \cdot (j_{u_n} + \Psi j_n) = j_n \cdot \nabla \Psi - \lambda \left(\frac{1}{T} - \frac{1}{T_n}\right)$$

or

$$\partial_t [u_n - n\Psi] + \nabla \cdot j_{u_n} = -\lambda \left(\frac{1}{T} - \frac{1}{T_n}\right) - n\dot{\Psi}\ .$$

They have proved the existence of solutions under some ad-hoc assumptions.

11 Appendix. Free energy

Because of the fundamental role which the free energy plays we want to point out that the expression (2.1) corresponds to the pertinent literature. The equilibrium distribution of electrons, their energy and free energy are described in

[19], chap. VIII, by

$$\begin{aligned}
\widetilde{N} &= N_D \frac{2}{2+\exp\frac{E_D-E_F}{kT}} + \sum_j \frac{Z_j}{1+\exp\frac{E_j-E_F}{kT}} \equiv N+n\ ,\\
U &= E_D N_D \frac{2}{2+\exp\frac{E_D-E_F}{kT}} + \sum_j \frac{Z_j E_j}{1+\exp\frac{E_j-E_F}{kT}}\ ,\\
F(\widetilde{N},T) &= \widetilde{N}E_F - kT\left\{N_D \log\left[1+2\exp\left(-\frac{E_D-E_F}{kT}\right)\right]\right.\\
&\quad \left. + \sum_j Z_j \log\left[1+\exp\left(-\frac{E_j-E_F}{kT}\right)\right]\right\}\ ,
\end{aligned}$$

where $\widetilde{N}=N+n$ denotes the number of electrons, Z_j are the occupation numbers, and E_F denotes the Fermi level. The free energy can be written as

$$\begin{aligned}
F(\widetilde{N},T) &= kTN\left\{\frac{E_F-E_D}{kT} - \frac{N_D}{N}\log\left[1+2\exp\left(-\frac{E_D-E_F}{kT}\right)\right]\right\} + NE_D\\
&+ \sum_j Z_j \left\{\frac{E_F}{1+\exp\left(\frac{E_j-E_F}{kT}\right)} - kT\log\left[1+\exp\left(-\frac{E_j-E_F}{kT}\right)\right]\right\}\ .
\end{aligned}$$

The first two summands on the right-hand side represent the free energy $F_D(N,T)$ of the electrons in the trap level. The variable $(E_D-E_F)/kT$ can be eliminated by means of

$$\frac{N}{N_D} = \frac{2}{2+\exp\frac{E_D-E_F}{kT}}$$

On this way the term $E_d(T)N + T\log\left[N^N(N_D-N)^{N_D-N}N_D^{-N_D}2^{-N}\right]$ arises. Let us write the expression for the free energy of electrons in the conduction band,

$$F_n(n,T) = kT\sum_j Z_j \left\{\frac{\frac{E_F}{kT}}{1+\exp\left(\frac{E_j-E_F}{kT}\right)} - \log\left[1+\exp\left(-\frac{E_j-E_F}{kT}\right)\right]\right\}\ ,$$

in our notation,

$$\begin{aligned}
F_n(n,T) = T\int \frac{v/T}{1+\exp\left[\frac{1}{T}\left(c_n|p|^{3/\alpha}+E_c-v\right)\right]}\,dp\\
- T\int \log\left[1+\frac{1}{\exp\left[\frac{1}{T}\left(c_n|p|^{3/\alpha}+E_c-v\right)\right]}\right] dp\ ,
\end{aligned}$$

and substitute $q :\equiv (c_n/T)|p|^{3/\alpha}$, $\chi = (v - E_c)/T$, and $M_c = (4\pi/3)\Gamma(\alpha+1)/c_n^\alpha$. On such a way we get

$$\begin{aligned}
F_n(n,T) &= nE_c + TM_cT^\alpha \frac{1}{\Gamma(\alpha)} \int_0^\infty \left[\frac{\chi}{1+e^{q-\chi}} - \log\left(1 + \frac{1}{e^{q-\chi}}\right) \right] q^{\alpha-1}\, dq \\
&= nE_c + TM_cT^\alpha \mathcal{F}_{\alpha-1}(\chi)\chi - TM_cT^\alpha \frac{1}{\Gamma(\alpha+1)} q^\alpha \log\left(1 + \frac{1}{e^{q-\chi}}\right)\Bigg|_0^\infty \\
&+ TM_cT^\alpha \frac{1}{\Gamma(\alpha+1)} \int_0^\infty q^\alpha \frac{-e^{\chi-q}}{1+e^{\chi-q}}\, dq \\
&= nE_c + Tn\mathcal{F}_{\alpha-1}^{-1}\left[\frac{n}{M_cT^\alpha}\right] - TM_cT^\alpha \mathcal{F}_\alpha \circ \mathcal{F}_{\alpha-1}^{-1}\left[\frac{n}{M_cT^\alpha}\right]
\end{aligned}$$

with $n = M_cT^\alpha \mathcal{F}_{\alpha-1}(\chi)$. The limits

$$\lim_{q\to+0} q^\alpha \log\left(1 + \frac{1}{e^{q-\chi}}\right) \;=\; 0^\alpha \log\left(1 + e^\chi\right) \;= 0$$

and

$$\begin{aligned}
\lim_{q\to+\infty} q^\alpha \log\left(1 + \frac{1}{e^{q-\chi}}\right) \;&=\; \lim_{q\to+\infty} \frac{\log\left(1 + \frac{1}{e^{q-\chi}}\right)}{q^{-\alpha}} \;=\; \lim_{q\to+\infty} \frac{-\frac{1}{1+e^{q-\chi}}}{-\alpha q^{-\alpha-1}} \\
=\frac{1}{\alpha} \lim_{q\to+\infty} \frac{q^{\alpha+1}}{1+e^{q-\chi}} \;&=\; \cdots \;=\; \frac{1}{\alpha}(\alpha+1)\alpha\cdots(\alpha-k) \lim_{q\to+\infty} \frac{q^{\alpha-k-1}}{e^{q-\chi}} \;=\; 0
\end{aligned}$$

$(-1 < \alpha - k - 1 \leq 0)$ vanish.

Remark 11.1 *Notice that the entropy of electrons in the conduction band,*

$$\begin{aligned}
S_n(n,T) &= \frac{1}{kT} \sum \frac{Z_jE_j}{1 + \exp\frac{E_j - E_F}{kT}} - \frac{E_F}{kT} \sum \frac{Z_j}{1 + \exp\frac{E_j - E_F}{kT}} \\
&+ \sum Z_j \log\left[1 + \frac{1}{\exp\frac{E_j - E_F}{kT}}\right] \\
&= \int \left[\frac{q-\chi}{1+e^{q-\chi}} + \log\left(1 + \frac{1}{1+e^{q-\chi}}\right)\right] dp \\
&= M_cT^\alpha \frac{1}{\Gamma(\alpha)} \int_0^\infty \left[\frac{q-\chi}{1+e^{q-\chi}} - (q-\chi) + \log\left(1 + e^{q-\chi}\right)\right] q^{\alpha-1}\, dq\ ,
\end{aligned}$$

coincides with the expression

$$\begin{aligned}
s[f_n] &= -\int \left[f_n \log f_n + (1 - f_n)\log(1 - f_n)\right] dp \\
&= -M_cT^\alpha \frac{1}{\Gamma(\alpha)} \int_0^\infty \left[\frac{1}{1+e^{q-\chi}} \log \frac{1}{1+e^{q-\chi}}\right. \\
&\qquad \left. + \left(1 - \frac{1}{1+e^{q-\chi}}\right) \log\left(1 - \frac{1}{1+e^{q-\chi}}\right)\right] q^{\alpha-1}\, dq
\end{aligned}$$

of an ensemble of electrons distributed in the phase space according to the equilibrium distribution

$$f_n(p) = \frac{1}{1+\exp\left[\frac{1}{T}\left(c_n|p|^{3/\alpha}+E_c-v\right)\right]}$$

(we have omitted the spatial coordinates as usual in this preprint).

Remark 11.2 *Notice that the expression of entropy of the preceding remark does not contain derivatives neither of the effective mass, i.e. of M_c, nor of the band edge E_c with respect to temperature, but remember that such derivatives guarantee that the entropy maximum principle yields the usual states of equilibrium.*

12 Appendix. Units and values.

We use dimensionless quantities only, but describe the physical units of the applied quantities in the following. We use the physical units A, cm, eV, g, K(elvin), sec, V, W, and some famous constants.

Constant	Symbol	Quantity
Boltzmann constant	k_B	$1.308 \times 10^{-23} Wsec/K$
dielectric permittivity of the vacuum	ϵ_{vac}	$8.854 \times 10^{-12} \frac{\text{V sec}}{\text{A cm}}$
electron rest mass	m_0	9.108×10^{-28} g,
elementary charge	q	1.602×10^{-19}A sec
Planck's reduced constant	$\hbar$	1.054×10^{-34} W sec^2

We choose, moreover, a reference temperature $\overline{T} \equiv \theta^*$K in Kelvin, such that all physical temperatures are $T_i\overline{T}$ or $T\overline{T}$.

We begin with a general observation. In physics quantities can be added or integrated only if they are measured in the same unit. For any more general functional relation $F = f(X, Y, ...)$ there is a group homomorphism $\varphi_f : R_+ \times R_+ \times ... \mapsto R_+$ such that $f(aX, bY, ...) = \varphi_f(a, b, ...) f(X, Y, ...)$. For integrals $G = \int f(X, ...)dX$ the relation $\int f(aX, ...)adX = a\varphi_f(a, ...)\int f(X, ...)dX$ holds and for a differential law $g = \frac{\partial f(X,...)}{\partial X} \equiv D_X f(X, ...)$ the relation reads $D_{(aX)} f(aX, ...) = \frac{1}{a}\varphi_f(a, ...) D_X f(X, ...)$. These observations help us to eliminate physical dimensions. Let $[X]$, $[Y]$, etc be units of X, Y, etc. Either $[f(X, Y, ...)] = \varphi_f([X], [Y], ...)$ is defined immediatly like $[G] = [X][f(X, ...)]$ or $[D_X f(X, ...)] = [f(X, ...)]/[X]$ or the unit $[F] \equiv \varphi_f([X], [Y], ...)$ is introduced formally. In any case the compatibility of diverse systems of units is warranted by the identity $\varphi_f(a[X], b[Y], ...) = \varphi_f(a, b, ...)\varphi_f([X], [Y], ...)$. This well known observation and the use of some scaled quantities permit us to get rid of the physical dimenions by $(F/[F]) = f(X/[X], Y/[Y], ...)$ (This procedure is often paraphrased by saying ’the electric charge is 1‘ etc, but we do not like this paraphrase.) We apply the following system of units.

Physical quantities	Notation	Unit
length		cm
particle densities	n_i, d, M_i, N_D	cm^{-3}
densities of energy	u, u_i, u_f, n_iE_i, c_L	$k_B\overline{T}/\mathrm{cm}^3$
density of entropy	s, s_f	$k_B/\ \mathrm{cm}^3$
scaled dielectric permittivity	ε	$\epsilon_{vac}k_B\overline{T}\ \mathrm{cm/q}^2$
scaled potentials or energies	ζ_i, $\widetilde{\zeta}_i$, ξ_i, $\widetilde{\xi}_i$, Ψ, E_i	$k_B\overline{T}$
effective masses	m_i	g

Notice that M_i and N_D are state densities which can be occupied temporarily by a particle, and the doping profile d counts the charge in elementary charges. The scaled potentials ζ_i, $\widetilde{\zeta}_i$, Ψ are the energies of the elementary charge in the corresponding potential; therefore we call ζ_i, $\widetilde{\zeta}_i$, Ψ potentials, what they really are. The potentials ξ_i and $\widetilde{\xi}_i$ are called ’reduced potentials‘. The ’energy density’ c_L is a scaled heat capacity per unit volume. The unit of the scaled dielectric permittivity is

$$\epsilon_{vac}k_B\overline{T}\mathrm{cm}/q^2 = 8854.\times(1.308/1.602^2)\times\theta^*(\mathrm{V/A})^2 = 4512.55\times\theta^*(\mathrm{V/A})^2\ .$$

As the state densities M_i represent only the effective masses m_i, we mention the connection

$$M_i(T) = 2\pi\left[\frac{\mathrm{cm}}{\hbar}\sqrt{2m_i(T)k_B\overline{T}}\right]^3 \ = \ 6.241\cdot 10^{17}\times[\theta^* m_i(T)/m_0]^{3/2}\ .$$

It has to be checked, whether a given set of material laws is thermodynamically consistent or in which domain of states the consistency holds. The criterium is the positivity of the heat capacity, $\partial_T u_f > 0$. We check a somewhat stronger condition for parabolic band structures ($\alpha_i = 3/2$) for systems without traps, i.e.

$$c_L + \sum_{l=1}^{2} q_l n_l T E_l'' > \sum_{l=1}^{2} n_l\left(\frac{2}{3}L_l(T)^2 + L_l(T) - TL_l'(T)\right)X_l^+$$

with $X_i^+ :\equiv \mathcal{F}_{3/2}\left[\frac{n_i}{M_i(T)T^{3/2}}\right]\Big/\mathcal{F}_{1/2}\left[\frac{n_i}{M_i(T)T^{3/2}}\right]$ (cf. Rem. 3.3). Moreover, we check the admissibility of carrier temperatures and the convexity of the negative conjugate potential of the entropy for parabolic band structures ($\alpha_i = 3/2$) for systems without traps, i.e. we ask whether the inequalities

$$\begin{aligned} a_0 - \sum_{l=1}^{2} \frac{b_l^2}{a_l} \equiv & c_L + \sum_{l=1}^{2} n_l q_l T E_l''(T) \\ & + \sum_{l=1}^{2} n_l Y_l^+ \left[L_l(T) + T L_l'(T) + \frac{2}{5} L_l(T)^2 \left(1 - \frac{2}{5 Y_l^+ Y_l^- - 3} \right) \right] \\ & > 0 \end{aligned}$$

and

$$A_0 - \sum_{l=1}^{2} F_l^T \mathbf{A}_l^{-1} F_l \equiv T^2 \left(a_0 - \sum_{l=1}^{2} \frac{b_l^2}{a_l} - 3 \sum_{l=1}^{2} n_l L_l(T)^2 \frac{Y_l^+}{5 Y_l^+ Y_l^- - 3} \right) \; > \; 0$$

with $Y_i^\pm \equiv: \mathcal{F}_{1/2\pm1}\left[\frac{n_i}{M_i(T) T_i^{3/2}}\right] \Big/ \mathcal{F}_{1/2}\left[\frac{n_i}{M_i(T) T_i^{3/2}}\right]$ are satisfied.

Example. $\theta^* = 300$, thermal voltage $U_{\overline{T}} = \frac{160.2}{3.924}$ V $= 40.8257$ V, Silicon (cf. [18]).

A rough approximation is a constant band gap of 1.12 eV. Since we do not have more specified informations about the diverse band edges, the formula $E_i(T) = E^* - q_i E_g(T)/2$ is chosen as an orientation. Thus $\sum_{l=1}^{2} q_l n_l E_l'' = -\frac{1}{2}(n_1 + n_2) E_g''(T)$.

Symbol	Quantity / Value
$E_g \overline{T} k_B$	$(1.1785 - .027075\,T - .02745\,T^2)$ eV
$E_g(T)$	$48.113 \cdot [1 - .02297\,T\,(1 + 1.014\,T)]$
$-T E_g''(T)/2$	$1.12063\,T$

Instead of the quantities for the total system we consider the situation of majority carriers and evaluate the quantities

$$F_l(n_l, T) := \frac{c_L}{n_l} + 1.12063\,T - \left(\frac{2}{3} L_l(T)^2 + L_l(T) - T L_l'(T) \right) X_l^+ \,,$$

$$\begin{aligned} G_l(n_l, T, T_l) := \frac{1}{n_l} \left(a_0^{(l)} - \frac{b_l^2}{a_l} \right) = & \frac{c_L}{n_l} + 1.12063\,T \\ & + Y_l^+ \left[L_l(T) + T L_l'(T) + \frac{2}{5} L_l(T)^2 \left(1 - \frac{2}{5 Y_l^+ Y_l^- - 3} \right) \right] \,, \end{aligned}$$

and

$$H_l(n_l, T, T_l) := \frac{1}{n_l}\left(a_0^{(l)} - \frac{b_l^2}{a_l}\right) - L_l(T)^2 Y_l^+ \frac{3}{5Y_l^+ Y_l^- - 3} \ .$$

They should be positive in interesting or realistic ranges of densities and temperatures. As we are mainly interested in the sign of these quantities we represent below the scaled quantity $\mathrm{Log}(H) := \mathrm{sign}(H) \log(1 + |H|)$.

Effective masses are given by fitting formulas $M(T) = a(1 + bT + cT^2)^{3/2}$. Thus we have

$$L(T) = TM'(T)/M(T) = \frac{3}{2}\frac{bT + 2cT^2}{1 + bT + cT^2}$$

and

$$\frac{2}{3}L(T)^2 + L(T) - TL'(T) = \frac{3T^2}{(1 + bT + cT^2)^2}\left(b^2 - c + 3bcT + 3c^2T^2\right) \ .$$

Symbol	Quantity / Value
$m_1(T)/m_0$	$1.045 + .135\,T$
$M_1(T)$	$3.464 \times 10^{21} \times (1 + .12919\,T)^{3/2}$
$L_1(T)$	$.193785T/(1 + .12919T)$
$L_1 - TL_1' + \frac{2}{3}L_1(T)^2$	$[.22376\,T/\,(1 + .12919\,T)]^2$
$m_2(T)/m_0$	$.523 + .420\,T - .133\,T^2$
$M_2(T)$	$1.2265 \times 10^{21} \times (1 + .803059\,T - .2543\,T^2)^{3/2}$
$L_2(T)$	$1.2046\,T \times (1 - .6333\,T)\,/\,(1 + .803059\,T - .2543\,T^2)$
$L_2 - TL_2' + \frac{2}{3}L_2(T)^2$	$[1.6424\,T/\,(1 + .803059\,T - .2543\,T^2)]^2$ $\times\,[1 - .6813\,T\,(1 - .31666\,T)]$

The scaled heat capacity of the lattice has the value

$$c_L = c \cdot \rho\mathrm{cm}^3/k_B = .703 \times 2.328/1.308 \times 10^{23} = 1.251 \times 10^{23}$$

such that the quantities should be evaluated for densities $n_l = 10^{23-\lambda}$ and temperatures $T \in [1/2, 4[$ between 150 K and 1200 K. The upper bound 1200 K is determined by a zero of $m_2(T)$!

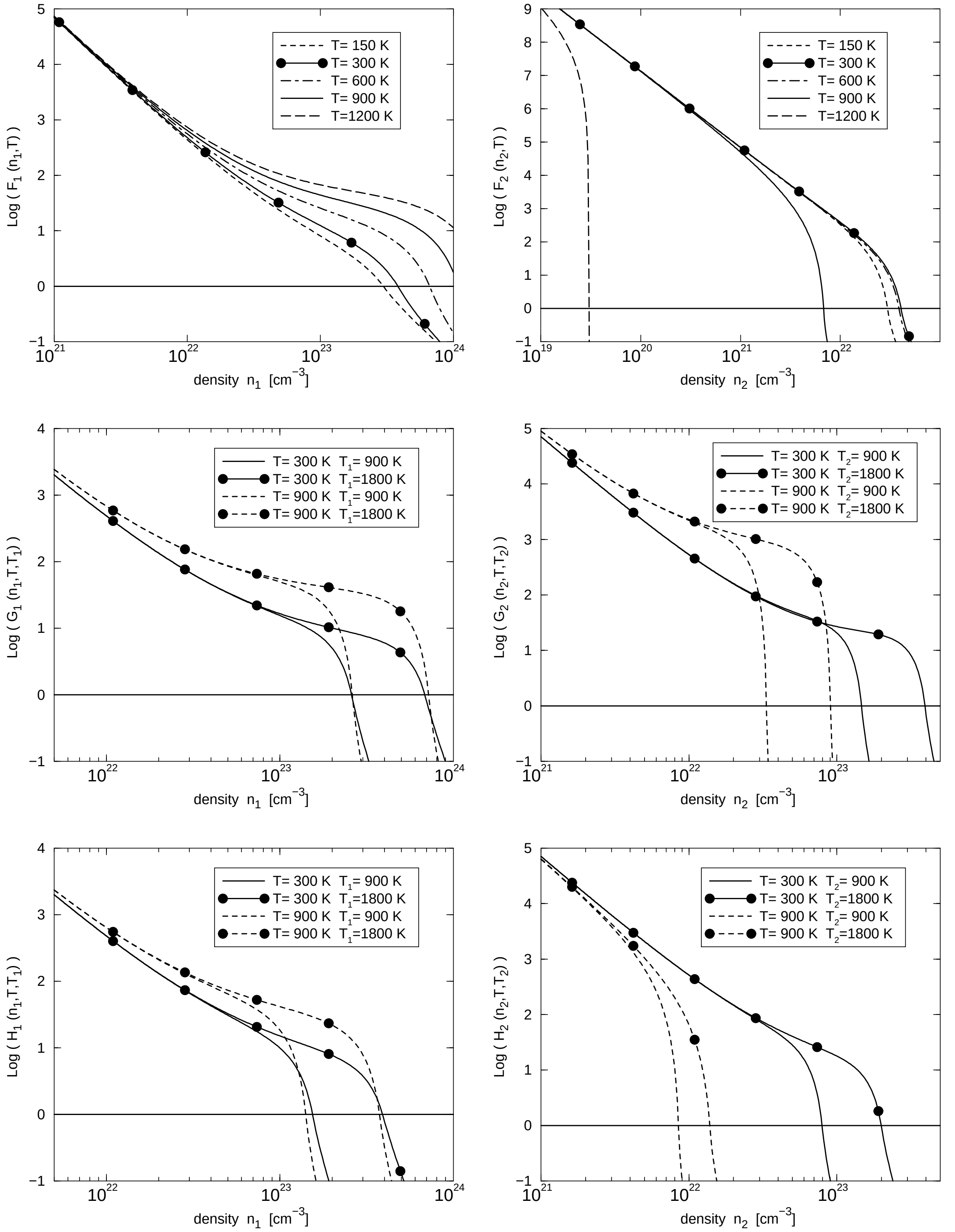

Fig. 1. The functions $Log(F_l)$, $Log(G_l)$ and $Log(H_l)$.

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