Non-equilibrium thermodynamic description of junctions in semiconductor devices

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Abstract

The methods of non-equilibrium thermodynamics of systems with an interface have been applied to the study of transport processes in semiconductor junctions. A complete phenomenological model for drift–diffusion processes in a junction has been derived, which includes, from first principles, both surface equations and boundary conditions, together with the usual drift–diffusion equations for the bulks. In this way, a self-consistent characterization of the whole system, bulks and interface, has been obtained in a common framework. The completeness of the model has been shown and a simple application to metal–semiconductor junctions developed.

1. Introduction

The phenomenological approach to semiconductor device modelling has proved to be very powerful and successful during the last decades. By means of a relatively simple set of equations (i.e., balance equations, constitutive relations, Maxwell equations), numerous devices have been modelled [1]. In spite of this success some aspects of the phenomenological models still remain not so well developed, namely the boundary conditions necessary to solve the set of phenomenological equations and the appropriate equations to describe the surface processes phenomenologically. These are by no means secondary problems in semiconductor devices, since the behaviour of most of the devices are critically affected by them. For instance, any device including a junction needs the appropriate boundary conditions, or discontinuity relations, to be imposed at the junction, as well as, the proper modelling of the superficial phenomena. In the term junction we also include the contacts used on the devices, whose effects may sometimes be relevant, for instance, in the development of semiconductor instabilities [2].

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Usually, these problems are discussed more or less intuitively, by invoking sometimes unclear physical arguments. We may say that, at this moment, in the current literature, a general phenomenological theory for boundary conditions and surface effects is lacking, although some valuable work has been published in this area [3]. It seems, therefore, desirable to propose phenomenological models that incorporate both boundary conditions and surface equations in a fundamental and general way. With such models, a self-consistent characterization of interfaces in semiconductor systems would then be able to be reached. Therefore, for a given junction, the models would provide the corresponding surface equations and boundary conditions appropriate for it simply by adjusting a few surface parameters. Clearly, from this point of view, semiconductor device modelling turns out to be a much easier task. Moreover, only with this kind of approach, the presently accepted models will be ultimately justified and, if necessary, improved in a systematic and general way.

As shown in [3], these kinds of models may be constructed by means of nonequilibrium thermodynamic arguments. In this paper, we will also make use of such an approach, but following a rather different formulation; namely, the one proposed in [6], in the context of fluid systems (see review [7] and references quoted therein). Non-equilibrium thermodynamic derivation of transport models have been widely used in the past for bulk systems [4], usually in the context of fluid systems, but also in the context of semiconductor systems [5]. For systems with interfaces, much less work has been done, although a rather complete theoretical treatment of this problem has already been published [7].

In this paper, we will present an application of such a formalism, to the derivation of a transport model for drift–diffusion processes in a junction. As required above, this model will incorporate, apart from the usual drift–diffusion equations for the bulk systems forming the junction, the appropriate boundary conditions and surface equations to respectively describe the coupling between the bulk systems and the surface processes. As mentioned, the entire model will be obtained in a systematic way, starting from very general considerations about the non-equilibrium thermodynamics behaviour of the system. For this reason, its generalization to include other irreversible processes may be obtained following the same procedure as the one presented here.

This paper is distributed as follows. In Section 2 we will discuss in detail the macroscopic description of the junction and the semiconductor model we will use throughout the paper. In Section 3 we will present and derive the phenomenological model, and consider some particularly interesting cases. The completeness of the model will be proved in Section 4, together with a simple application to a metal–semiconductor junctions. Finally, in Section 5 we will summarize our main results.

2. Macroscopic description of a junction

From a macroscopic point of view, a junction may be defined as the very narrow region that exists between two semiconductors in contact, and which exhibits peculiar
macroscopic behaviour reflected in the fact that the equations of state, transport coefficients, etc. are different from those of the bulks. It is clear that due to the possibility of jumps in the relevant quantities, a description of the system in terms of variables varying continuously from one region to the other is not appropriate. Therefore, it is necessary to find the jump relationship coupling the different parts, in terms of the interfacial properties.

To this end we will introduce in our system a geometrical surface inside the interfacial region that divides the system in two separate parts, referred to as the bulk parts, which will be denoted by $-$ and $+$. We assume that each of these bulk parts behaves macroscopically as in the absence of interface. Of course, this behaviour will be different from the real one inside the interfacial region. To take this fact into account one introduces surface variables, denoted by the superscripts $s$, defined only at the geometrical surface. These variables are the appropriate to describe the interfacial region.

The precise definition of these surface variables runs as follows. Let $\theta^+(\theta^-)$ be Heaviside's functions whose values are 1 (0) for points located on the right (left) of the surface and 0 (1) for the opposite case. Let $d$ be an unspecified field and $d^\pm$ be the corresponding fields in the bulks, referred to as the extrapolated fields. As pointed out before, these fields differ from the real ones in the interfacial region. To account for this difference we introduce excess fields $d_{ex}$ as follows [7]:

$$d_{ex}(r) = d(r) - d^+(r)\theta^+(r) - d^-(r)\theta^-(r).$$

These excess fields have, by definition, two important properties: (1) They vanish away from the interfacial region, because there the effects of the interface die out, and consequently the real fields and the bulk ones coincide. Thus the excess fields are only defined in the interfacial region. (2) They take small values when interfacial effects are small, that is, when the real fields do not depart significantly from the extrapolated ones.

The surface variables are defined as averages of the excess fields. For a planar surface at rest identified with the plane $x = 0$, we can write [10]

$$d_x(y, z) = \int dx d_{ex}(r),$$

where the integration may be extended outside of the interfacial region, for the excess fields vanish very quickly there. These fields constitute the relevant quantities in the description of continuum systems in the presence of interfaces, as was first pointed out in Ref. [8].

Note that, with this characterization, the system is seen as composed by three sub-systems: two bulks, with unchanged properties just until the geometrical interface and described by means of the extrapolated variables, and an interface, accounting for the properties of the interfacial region through the surface variables.

As noted before, in this paper we will follow a thermodynamic approach. This forces us to give an a priori thermodynamic characterization of the systems involved.
Here we will assume that the bulk subsystems belong to the class of the multicomponent electrically conducting polarizable fluids whose thermodynamic variables are: the densities of internal energy, \( u \), and entropy, \( s \), the number density of each component, \( n_k \), and the electric polarisation \( P \) (magnetic polarisation, \( M \), may also be included). The surface subsystem will belong to the same class, but neglecting any polarisation phenomena. The bulk system densities will be defined per unit of volume while at the surface per unit of area.

This semiconductor fluid-like model we will use throughout this paper is very much related to the one proposed in Ref. [3] in which a semiconductor may be considered as the superposition of three continuum media, namely the crystal lattice, the electrons and the holes. The first one is, in general, positively or negatively charged depending on the sign of the ionised impurities. It will be considered at rest with fixed mass and impurity densities, not including for example any aging phenomena. This subsystem is mainly responsible for the polarisation effects. Electrons and holes will be considered charged fluids. For the sake of simplicity, we will assume that each component has the same charge and mass on each side of the junction. This assumption considerably simplifies our analysis in the sense that we are reducing the number of constituents in our description.

It is worth noting that although the formalism we present applies to semiconductor systems, it can also be used to study other kinds of materials, like metals or insulators, because from the thermodynamic point of view, they have similar characteristics. It is only when the state equations are specified that the differences become substantial.

3. Non-equilibrium thermodynamics model for a junction

Once the thermodynamic description of the junction has been established, we can now proceed to investigate the non-equilibrium behaviour of the whole system by applying the usual methods of non-equilibrium thermodynamics [4]. Our main purpose in this section will be to obtain the constitutive relationships for the irreversible processes in the bulk and at the interface together with boundary conditions coupling the different parts of the system. As noted before, a similar approach was previously proposed in Ref. [9] in the context of fluid systems.

Although the calculations may be worked out in the very general case, by including all possible irreversible processes as in Ref. [9], we will consider, for the sake of simplicity and clarity, only the drift and diffusion processes, neglecting the recombination or generation processes, magnetic effects, thermal processes or relaxation polarisation processes. The last three may be introduced in a more or less straightforward way by following the procedure presented in this paper. Generation–recombination processes deserve special treatment in the framework of non-equilibrium thermodynamics, due to the intrinsic non-linear nature of the constitutive relations [4].
Moreover, we will also consider a one-dimensional system in which significant variations of the relevant quantities used in its description occur only in a direction perpendicular to the interface. Vectorial fields will then have components along the normal to the junction, and the vectorial notation will be suppressed.

3.1. Basic equations of the model

This subsection is devoted to the introduction of the complete set of equations that constitutes the model, leaving its rigorous derivation for next subsection. As mentioned in the introduction, the equations of the model may be divided in three categories making reference to bulk, surface, and boundary conditions, respectively:

(i) Bulk equations. The equations describing the bulks consist of balance equations, constitutive relations and Poisson’s equation, supplemented by the corresponding equations of state. They have been found to be

\[ \frac{\partial n_k^\pm}{\partial t} + \frac{\partial J_k^\pm}{\partial x} = 0, \quad k = 1, 2, \quad (3) \]

\[ \frac{\partial n_3^\pm}{\partial t} = 0, \quad (4) \]

\[ \frac{\partial D_k^\pm}{\partial x} = q_k^\pm, \quad (5) \]

\[ J_k^\pm = -D_k^\pm \frac{\partial n_k^\pm}{\partial x} + \left( -1 \right)^k \mu_k^\pm n_k^\pm E^\pm, \quad k = 1, 2, \quad (6) \]

where \( n_k^\pm \) is the particle number density with the index \( k \) referring to the subcontinua electrons \((k = 1)\), holes \((k = 2)\) and lattice \((k = 3)\), \( q^\pm = \sum_{k=1}^{3} q_k n_k^\pm \) is the total density charge, with \( q_k \) the charge of the \( k \)th component, \( D^\pm \) is the electric displacement, \( J_k^\pm \) is the particle number density current, \( \mu_k^\pm \) is the diffusion coefficient of \( k \)th component, and \( \mu_k^\pm \) the corresponding mobility. These two last quantities are related through Einstein’s relation

\[ \frac{D_k^\pm}{\mu_k^\pm} = \frac{\partial \mu_k^\pm}{\partial n_k^\pm} \frac{n_k^\pm}{e}, \quad k = 1, 2, \quad (7) \]

where \( e \) is the (positive) electron charge. These bulk equations constitute the usual drift–diffusion model for a semiconductor when generation–recombination processes are neglected [1] (Eq. (4) simply states that the aging phenomena are neglected). Eq. (6) can be rewritten in a more appealing form by introducing the electrochemical potential for the \( k \)th component as

\[ \phi_k^\pm = \mu_k^\pm + q_k V^\pm, \quad k = 1, 2, \quad (8) \]
with the electric potential defined as usual by \( E^\pm = -\partial V^\pm /\partial x \). For the constitutive relations, one then obtains
\[
e J_k^\pm = -n_k^\pm \mu_k^\pm \frac{\partial \phi_k^\pm}{\partial x}, \quad k = 1, 2, \tag{9}\]
which shows that, for drift–diffusion processes, the electrochemical potentials (usually called quasi-Fermi levels) play an important role, as we will see later when boundary conditions are expressed in a natural way in terms of these potentials.

The appropriate equation of state for the bulk systems corresponding to the model presented are
\[
\mu_k^\pm = \mu_k^{\pm,0} (n_k^\pm), \quad k = 1, 2, \tag{10}\]
\[
D^\pm = \varepsilon^\pm E^\pm, \tag{11}\]
where \( \varepsilon^\pm \) are the bulk dielectric permitivities, assumed to be independent of \( n_k^\pm \). For the case of non-degenerate semiconductors one has for the first state equations
\[
\mu_k^\pm = \mu_{k,0}^{\pm} + k_B T \ln \left( \frac{n_k^\pm}{N_k^\pm} \right), \quad k = 1, 2 \tag{12}\]
where \( \mu_{k,0}^{\pm} \) is a chemical potential of reference, with \( N_k^\pm \) being the effective density of states in the conduction \((k = 1)\) and valence \((k = 2)\) band. In that case Einstein’s relation reduces to its usual expression \([1]\),
\[
\frac{D_k^\pm}{\mu_k^\pm} = \frac{k_B T}{e}, \quad k = 1, 2. \tag{13}\]

(ii) Surface equations. As for the bulk, surface equations would consist in general of balance equations, constitutive relations and state equations. For the case of a one-dimensional system no surface constitutive relations are needed, because no transport process takes place along the surface. In that case, we then simply have
\[
\frac{\partial n_k^\pm}{\partial t} + [J_k]_r = 0, \quad k = 1, 2, \tag{14}\]
\[
\frac{\partial n_k^\mp}{\partial t} = 0, \tag{15}\]
where \( n_k^\pm \) is the surface density number of the \( k \)th component, and where we have defined \([A]_r = A^+ - A^-\), with \( A^\pm \) being evaluated at the interface. Again Eq. (15) states that no aging phenomena are allowed, now at the interface. Moreover, the surface state equations are in that case simply
\[
\mu_k^\pm = \mu_k^\pm (n_k^\pm), \quad k = 1, 2. \tag{16}\]
Remember that we are assuming that the interface is non-polarizable and hence no surface state equation for the surface polarisation is necessary (see the appendix).
(iii) Boundary conditions. For the boundary conditions, we have to distinguish between the ones corresponding to Poisson’s equation and the ones that correspond to the drift diffusion processes. The former ones may be written as

\[ [D]_– = q^s, \quad (17) \]

\[ [V]_– = 0, \quad (18) \]

where \( q^s = \sum_{k=1}^{3} q_k n_k^t \) is the net surface charge, whereas for the latter we have obtained

\[ J_k^± = -\frac{1}{T} F_k^± (\{\phi^+_j - \phi^-_j\}, \{\phi^+_j - \phi^-_j\}), \quad k, j = 1, 2, \quad (19) \]

where \( \phi_k^t = \mu_k^t + q_k [V]_– \) is the electrochemical potential of the \( k \)th component at the surface, with \( [A]_– = 1/2(A^+ + A^-) \), and where all the bulk magnitudes are evaluated at the interface, that is, at \( x = 0 \).

These equations can be formulated in a more compact way, by introducing a simplified notation for the differences of electrochemical potentials,

\[ X_k^± = \phi_k^+ - \phi_k^–, \quad (19) \]

\[ J_k^± = (J_1^+, J_2^±) \]

where \( 1 \) and \( 2 \) refer to electrons and holes, respectively. The scalar product of two such vectors will then read \( J^+ \cdot X^+ = \sum_{k=1}^{2} J_k^+ X_k^+ \). In this notation, Eq. (19) can be written simply as

\[ J^± = -\frac{1}{T} F^± (X^+, X^–). \quad (20) \]

The boundary conditions for the drift–diffusion processes, Eq. (19) or Eq. (20), deserve some comments. First of all, it should be noted that they are non-equilibrium boundary conditions, that is, they relate the discontinuities in the relevant quantities in the drift–diffusion process, namely the electrochemical potentials to the currents. Moreover, although they have been formulated in terms of currents and forces (see above), they may also depend on the surface thermodynamic variables (see next subsection). Finally, the functions \( F_k^± \) are subject to certain thermodynamic restrictions, namely,

\[ F^± (0, 0) = 0, \quad (21) \]

\[ X^+ \cdot F^+ + X^- \cdot F^- \geq 0, \quad (22) \]

\[ \frac{\partial F_k^±}{\partial X_j^±}_{eq} \leq \frac{\partial F_j^β}{\partial X_k^±}_{eq}, \quad k, j = 1, 2, \quad \alpha, \beta = +, –, \quad (23) \]

coming from the equilibrium condition, the second principle of thermodynamics, and the Onsager’s symmetries, respectively. Note that we have \( \frac{1}{2} n(n-1) \) symmetry relations, where \( n \) is the number surface thermodynamic forces (in the general case \( n = 4 \)).
It should be noted that for the model presented above, the total electric density current is a continuous field through the interface. Indeed, from Eqs. (14) and (15), the total surface charge equation for a one-dimensional system is found to be

$$\frac{\partial}{\partial t} q_k + [J_c] = 0,$$

(24)

where $J_c = \sum_{k=1}^{3} q_k J_k^\pm$, is the total electric conducting density current. Upon substituting Eq. (17) in Eq. (24), we obtain

$$[I] = 0,$$

(25)

where

$$I^\pm = \frac{\partial}{\partial t} D^\pm + J_c^\pm$$

(26)

is the total electric density current which can be shown, from the semiconductor bulk equations, to be only function of time (Ampere’s law). This fact and Eq. (25) make the use of a superindex for this quantity irrelevant.

### 3.3. Entropy production and constitutive equations

Our purpose in this subsection is to justify the equations proposed in the previous subsection.

(i) For the bulk equations we only have to derive the constitutive relations, Eq. (6), and Einstein’s relation Eq. (7), because Eqs. (3) and (4) are simply continuity equations and Eqs. (10) and (11), appropriate state equations. More general equations of state would be possible a priori, but we will conclude from our analysis that these are the consistent ones with the remaining equations of the model. To derive the constitutive relations, we will analyse the bulk entropy productions using the methods of non-equilibrium thermodynamics [4]. In the case concerning us, that is when only drift–diffusion processes are considered, the entropy production reduces to (see the appendix)

$$\sigma_k^\pm = -\frac{1}{T} \sum_{k=1}^{3} J_k^\pm \left( \frac{\partial \mu_k^\pm}{\partial x} - q_k E^\pm \right),$$

(27)

where the quantities $J_k^\pm$ are diffusion currents defined in the appendix. After applying Prigogine’s theorem [4], for which we can redefine the diffusive fluxes with respect to any desired velocity (in our case we will take the reference frame fixed to the lattice continuum which is assumed to be at rest), Eq. (27) transforms into

$$\sigma_k^\pm = -\frac{1}{T} \sum_{k=1}^{3} J_k^\pm \left( \frac{\partial \mu_k^\pm}{\partial x} - q_k E^\pm \right).$$

(28)
From it we can infer the phenomenological constitutive relations. For bulk processes they are well represented through linear relations, that is,

$$J_k^\pm = -\frac{1}{T} \sum_{j=1}^{2} L_{kj}^\pm \left( \frac{\partial \mu_{j}^\pm}{\partial \chi} - q_j E^\pm \right), \quad k = 1, 2,$$

(29)

where $L_{ij}^\pm$ is the matrix of phenomenological coefficients which according to Onsager’s principle is symmetric and according to second law positive definite \[4\], and only depends on the bulk thermodynamic variables, which in our case are, for instance, $T^\pm, n_k^\pm, E^\pm$. To arrive at the form given in Eq. (6) we will suppose that the cross effects are negligibly small, $L_{12}^+ = L_{21}^- \approx 0$ and that the phenomenological coefficients and the chemical potentials do not depend on $E^\pm$. We will also assume that the chemical potentials depend only on the corresponding density, that is, $\mu_k^\pm = \mu_k^\mp (n_k^\pm)$. Then defining the diffusion coefficient and the mobility for the electrons and holes as

$$D_k^\pm = \frac{L_{kk}^\pm}{T} \frac{\partial \mu_k^\pm}{\partial n_k^\pm}, \quad k = 1, 2,$$

(30)

$$\mu_k^\pm = \frac{L_{kk}^\pm}{T} \frac{e}{n_k^\pm}, \quad k = 1, 2,$$

(31)

Eq. (29) transforms into the drift–diffusion relation given in Eq. (6).

Einstein’s relation, Eq. (7), follows directly from the previous definitions of the diffusion and mobility coefficients. On the other hand, taking into account the definition of the electrochemical potential given in Eq. (8), we may rewrite Eq. (29) as

$$J_k^\pm = -\frac{1}{T} \sum_{j=1}^{2} L_{kj}^\pm \frac{\partial \phi_k^\pm}{\partial \chi}, \quad k = 1, 2,$$

(32)

which after neglecting cross effects and considering the definition of the mobility given through Eq. (31), transforms into Eq. (9).

(ii) The surface equations (14) and (15) are the corresponding one-dimensional surface continuity equations and they have been derived in the appendix. As before, Eq. (10) corresponds to particular forms of the surface state equations appropriate to the model.

(iii) Finally, let us focus on the boundary conditions. Eqs. (17) and (18) are the usual discontinuity relation for Poisson’s equation and they do not deserve further comments (see the appendix for the case in which surface polarisation is included in the formulation and Ref. [10] for a general treatment of Maxwell’s equations).

To derive the remaining boundary conditions, Eq. (19), we proceed, as we did in the bulk, by analysing the surface entropy production. It is shown in the appendix that for the case of drift–diffusion processes, it may be written as

$$\sigma_s^\pm = -\frac{1}{T} \sum_{k=1}^{2} \left[ J_k (\mu_k - \mu_k^\pm) \right].$$

(33)
Using the definition of the bracket \([\cdot \cdot]_\) we may rewrite Eq. (33) as

\[
\sigma^*_s = -\frac{1}{T} \sum_{k=1}^{2} J^+_k (\mu^+_k - \mu^-_k) - \frac{1}{T} \sum_{k=1}^{2} J^-_k (\mu^-_k - \mu^+_k). \tag{34}
\]

Finally, by using Eq. (18) and the definition of the surface and bulk electrochemical potentials given in the previous subsection, we arrive at our final expression for the surface entropy production

\[
\sigma^*_s = -\frac{1}{T} \sum_{k=1}^{2} J^+_k (\phi^+_k - \phi^-_k) - \frac{1}{T} \sum_{k=1}^{2} J^-_k (\phi^-_k - \phi^+_k) \tag{35}
\]

\[
= -\frac{1}{T} J^+ \cdot X^+ - \frac{1}{T} J^- \cdot X^- \tag{36}
\]

This last expression enables us to identify the surface currents, \(J^\pm\), and their conjugated surface thermodynamic forces, \(X^\pm\) in a clear way; hence, we can propose the phenomenological relations between them. As we will see in the application, for interfaces, general kinds of phenomenological relations need to be used, and for that reason we have written them like in Eq. (20), where the dependence of the functions \(F^\pm\), on the surface thermodynamic variables, \(T, n^\pm\), is implicit.

Equilibrium and non-equilibrium thermodynamic considerations impose some restrictions on the functions \(F^\pm\), namely:

(a) At equilibrium, all thermodynamic fluxes and forces must vanish, which leads to the requirement that \(F^\pm\) have to vanish in equilibrium, that is, \(F^\pm(0,0) = 0\).

(b) They have to be defined in such a way as to make surface entropy production positive definite, in accordance with the second law of thermodynamics, that is, \(X^+ \cdot F^+ + X^- \cdot F^- \geq 0\) (see Eqs. (36) and (20)).

(c) Near equilibrium, in which linear phenomenological relations hold, the matrix of phenomenological coefficients satisfy Onsager’s reciprocal relations. This matrix is precisely the Jacobian matrix for the functions \(F^\pm\) evaluated at equilibrium and, consequently, it must have the corresponding symmetry properties.

These three requirements are, in fact, the conditions expressed through Eqs. (21)–(23).

3.3. Particular cases

3.3.1. Steady conditions

Under steady conditions, the model presented in Section 3.1 and in particular the boundary conditions simplify considerably, and they can be written in a more useful form for practical applications. Indeed, from Eq. (14) we conclude that no discontinuity in the conducting currents occurs across the interface, that is, \(J^+=J^-\) at the interface. Hence, after identifying the terms of the right-hand sides in Eq. (20) and solving for one of the two forces, we can write the boundary conditions
in the form
\[ X^- = G^+ (X^+) , \]  
\[ J^+ = - \frac{1}{T} H^+ (X^+) , \]  
where \( G^+ \) is a function satisfying the relation
\[ F^+ (X^+, G^+ (X^+)) = F^- (X^+, G^+ (X^+)) \]  
and \( H^+ \) is given by
\[ I^+ (X^+) = F^+ (X^+, G^+ (X^+)) . \]  
It can be seen that the general restrictions mentioned previously require that
\[ G^+(0) = H^+(0) = 0 \]  
and that
\[ (X^+ + G^+ (X^+)) \cdot H^+ (X^+) \geq 0 \]  
for all values of \( X^+ \).

This last relationship is more naturally expressed by using the discontinuities in the bulk electrochemical potentials, \([\phi]_-\), as the independent variables. In this case, by taking into account that \([\phi]_- = X^+ + X^-\), we may rewrite Eqs. (37) and (38) as
\[ J^+ = - \frac{1}{T} F_1 ([\phi]_-) , \]  
\[ X^+ = F_2 ([\phi]_-) , \]  
where \( F_2 \) satisfies
\[ G^+ (F_2 ([\phi]_-)) + F_2 ([\phi]_-) = [\phi]_- \]  
and \( F_1 \)
\[ F_1 ([\phi]_-) = H^+ (F_2 ([\phi]_-)) . \]  
Now the thermodynamic restrictions are simply
\[ F_2 (0) = F_1 (0) = 0 \]  
\[ [\phi]_- \cdot F_1 ([\phi]_-) \geq 0 . \]  
The steady state boundary conditions expressed through Eqs. (42) and (43), have the appropriate form to be used in practical calculations, as we will show in future works.

3.3.2. No surface states

Our purpose in this subsection is to present the simplified version of the model corresponding to the case in which the surface number densities vanish, that is, when \( n_i^+ = 0 \) for \( i = 1, 2, 3 \). This case may be related to the case in which there are no surface, or interfacial, states. The first simplification comes from the fact that now we obviously do not need a surface state equation like Eq. (16). Moreover, from the
surface continuity equations, Eq. (14), we can see that the number density currents are continuous across the interface, that is, \([J]_- = 0\). Finally, it can be shown that the entropy production corresponding to this situation can be obtained from Eq. (33) by simply imposing \([J]_- = 0\) on it. One then arrives at

\[
\sigma^x_s = -\frac{1}{T}\frac{1}{[\phi]_-} \cdot J^+.
\] (48)

From this expression we see that, in this case, we obtain a single discontinuity relationship, which can be written as

\[
J^+ = -\frac{1}{T}M([\phi]_-)
\] (49)

instead of the two obtained in the general case Eq. (20) or Eqs. (42) and (43) in the steady case. As before, \(M\) is subject to some thermodynamic restrictions, namely

\[
M(0) = 0,
\] (50)

\[
[\phi]_- \cdot M([\phi]_-) \geq 0,
\] (51)

\[
\left. \frac{\partial M_1}{\partial [\phi_2]} \right|_{eq} = \left. \frac{\partial M_2}{\partial [\phi_1]} \right|_{eq}
\] (52)

coming from the equilibrium condition, the second principle of thermodynamics and the Onsager's symmetries.

4. Application of the model

In this section we will first show, in a more or less heuristic way, that the model presented along this paper is complete (see below). For simplicity's sake we will focus on unipolar systems, but similar arguments can be applied to bipolar systems. As an example of application, we will show that the thermionic emission–diffusion theory for metal–semiconductor (M–S) abrupt junctions [1], is a thermodynamically consistent model, because it can be fitted into the framework of the present model. Similar arguments may be used to analyse more complicated situations, in which not only thermodynamic consistency is expected to be proved, but also a generalization of the corresponding models will be derived.

4.1. Completeness of the model

What will be proved in this subsection is that if the unspecified phenomenological equations, Eqs. (16) and (20) in the general case or Eq. (49) in the non-surface state case, are given explicitly and the physical conditions at infinity are specified, then we can find the solution of the model. By physical conditions at infinity, we mean those conditions that one assumes the solution must satisfy far away from the interface. For
instance, for infinite systems, one assumes that the interfacial effects die out at infinity, and hence that the system is locally neutral there, that is, \( n_e^+ \to n_0^+ \) and \( \partial n_e^+/\partial x \to 0 \) for \( x \to \pm \infty \), where we have assumed the single carriers to be electrons (subindex \( e \)) and the donor density (subindex \( 0 \)) to be uniform. For finite systems, one assumes that, at a certain distance away from the interface, the interfacial effects have nearly died out, and, therefore, one searches for an approximate solution that satisfies this condition.

In any situation, our model provides the corresponding solutions. To see this, let \( x_0^- \) be, for the moment, two unspecified points, at which the neutrality conditions are satisfied within a certain degree of approximation, that is,

\[
\begin{align*}
n_e^+ (x_0^+, t) &= n_0^+ + \Delta_1^+ , \\
\frac{\partial n_e^+ (x_0^-, t)}{\partial x} &= \Delta_2^+ ,
\end{align*}
\]

where \( \Delta_{1,2}^+ \) take small values (for infinite systems these precise values are not important, for at the end of the argument one tends them to zero). Note that by taking Eqs. (53) and (54) as boundary conditions, one can solve the semiconductor bulk equations, Eqs. (3), (5) and (6). A simple way to do this is note that these equations can be transformed into a single equation for the electric field, see for instance Ref. [11],

\[
\frac{\partial E^\pm}{\partial t} - D_e^\pm \frac{\partial^2 E^\pm}{\partial x^2} - \mu^\pm E^\pm \left( \frac{\partial E^\pm}{\partial x} - \frac{e}{\varepsilon^\pm n_0^\pm} \right) = \frac{I}{e^\pm} ,
\]

where \( I \) is the total electric density current, and that Eqs. (53) and (54) can be rewritten as

\[
\begin{align*}
\frac{\partial E^\pm (x_0^+, t)}{\partial x} &= \vec{A}_1^+ , \\
E^\pm (x_0^+, t) &= \frac{1}{\sigma^\pm} J_e^\pm (x_0^+, t) + \vec{A}_2^+ ,
\end{align*}
\]

where Eqs. (5) and (6) have been used. In Eqs. (56) and (57), \( \sigma^\pm = e\mu^\pm n_0^\pm \) are the bulk conductivities, and \( \vec{A}_{1,2}^+ \), two very small quantities, related to \( \Delta_{1,2}^+ \).

Once one has solved for the semiconductor bulk equations (usually numerically), one can compute some useful quantities like \( J_e^\pm (0, t) \), \( n_e^\pm (0, t) \), \( \mu_e^\pm (0, t) \), \( V^\pm (0, t) - V^\pm (x_0^+, t) \), \( \phi_e^\pm (0, t) - \phi_e^\pm (x_0^+, t) \), ... by simply using the bulk equations again. Note that all these quantities will obviously be dependent on \( x_0^+ \), \( I(t) \) and \( \vec{A}_{1,2}^+ \).

If surface states are present, one can then compute the corresponding expressions for the surface quantities, \( q^s(t) \) and \( \mu_e^s(t) \) as functions of \( x_0^+ \), \( I \) and \( \vec{A}_{1,2}^+ \). This can be done as follows: from Poisson’s equation, Eq. (5), and the discontinuity equation, Eq. (17), one has

\[
E^+ (x_0^+, t) - E^- (x_0^-, t) = q^- (t) + q^+ (t) + q^s (t) ,
\]
where we have defined

\[ q^\pm = \pm \frac{e}{e^2} \int_0^{x^\pm_0} (n_0^\pm - n_e^\pm) \, dx. \]  

(59)

From Eq. (58) one obtains \( q'(t) \), for it is the only unknown quantity in this expression. By using the surface state equation, Eq. (16), one can then derive the corresponding expression for \( \mu_e(t) \) (we assume that the surface donor density, \( n_0^s \), as well as the bulk ones, \( n_0^b \), are known).

All the previous results suffice to derive the expressions for \( x_e^\pm (0, t) \) and \( J_e^\pm (0, t) \) in terms of \( x_0^\pm, I \) and \( \mathcal{A}_{1,2}^\pm \). By substituting them into the discontinuity relationships, Eq. (20), one then obtains a system of two equations, which allows one to derive the expressions for \( x_0^\pm \) as functions of \( I \) and \( \mathcal{A}_{1,2}^\pm \). At this point one is then able to eliminate the dependence of all the previous results on \( x_0^\pm \). As a result, all these magnitudes become only functions of \( I \) and \( \mathcal{A}_{1,2}^\pm \).

For an infinite system, one then tends \( \mathcal{A}_{1,2}^\pm \) to zero (and consequently \( x_0^\pm \) will tend to \( \pm \infty \)). The resulting expressions, which are now only functions of \( I \), constitute the searched solution of the model.

For a finite system, one assumes that the results found with finite values for \( \mathcal{A}_{1,2}^\pm \) are the (approximate) solutions for the active region of the device, and that the remaining parts of the system behave as in the absence of the interface. We then arrive at the desired solution in this case. In some cases, for instance for short devices, this is not a good approach, and a more elaborate one must be carried out [14]. In any case, it can be shown that the correct implementation of the model gives the corresponding solution.

For the particular case in which there are no surface states present, the same derivation holds, by simply noting that in this case one has \( q'(t) = 0 \). Therefore, Eq. (58) constitutes the first equation to determine \( x_0^\pm \), and the second one is the single discontinuity relation for that case, Eq. (49).

4.2. Thermionic emission–diffusion theory for M–S junctions

The thermionic emission–diffusion theory for abrupt M–S junctions without interface states is a currently accepted model to describe the rectifying properties of M–S junctions when the main limiting current mechanisms are the thermionic emission of carriers over the junction barrier and the diffusion of the carriers inside the semiconductor [1,12]. Our purpose in this subsection is to show that this model can fit into the framework of the model presented throughout this paper, and that, as a consequence, it is a thermodynamically consistent model.

As in many cases, this model assumes drift–diffusion transport equations for the bulks [1], which are equivalent to the ones presented in Section 3. On the other hand, it also assumes the following boundary condition to describe the thermionic emission
processes [13] (see also Ref. [1]):
\[ eJ^+_e = V_R(n_m - n^+_e), \]  
(60)
where \( V_R \) is a positive constant, and \( n_m = N^+_C \exp\{-[e/(k_BT)]\phi^+_e\}. \) This boundary condition is a thermodynamically consistent, in the sense of the present paper. Indeed, by using Eq. (12) it can be rewritten in the form of a discontinuity relation
\[ eJ^+_e = I_T e^{-[e/(k_BT)]\phi^+_e(e^{[1/(k_BT)]}\phi^-_e - 1)}, \]
(61)
where \( I_T = V_R N^+_C \). Furthermore, this discontinuity relation clearly satisfies the thermodynamic restrictions derived for that case, Eqs. (50) and (51) (for unipolar systems without interface states there are no symmetry relationships). It is worth noting that although Eq. (50) is expected to be satisfied for all the models Eq. (51) might not, for its origin is purely thermodynamic, and it has not been included, as far as we know, in any phenomenological model. Moreover, it should be pointed out that the constitutive relation given through Eq. (61) is effectively non-linear (as we have assumed to be), in the sense that it does not relate the current and the force linearly. However, this does not constitute a singular case in non-equilibrium thermodynamics for there are different irreversible processes (chemical reactions [4], adsorption processes [21], ... ) which display such non-linear behaviours.

Similar analysis may be carried out for more complicated models, for instance those including interface states. By fitting those models into the framework of our model their thermodynamic consistency may be established and, what is more important, their generalization eventually derived. These facts illustrate the power of the application of the thermodynamic methods to semiconductor systems.

5. Conclusions

In this paper, we have presented a fully macroscopic, and thermodynamically consistent, derivation of a phenomenological one-dimensional model for drift–diffusion processes in a junction. The model, which consists of the usual transport equations for the bulk systems that conform the junction, also incorporates the appropriate boundary conditions or discontinuity relationships, and the equations describing the surface phenomena. These last two ingredients are essential from a fundamental point of view, and they allow a complete modelling of semiconductor devices, in which junctions play a so relevant role.

The derivation of the model has been completely based on thermodynamic arguments. A first step has consisted of thermodynamically characterising the junction, by means of the introduction of the surface and (extrapolated) bulk variables. Therefore, the methods of non-equilibrium thermodynamics for systems with interfaces [7] have been applied giving rise directly to the above-mentioned model. It is worth noting that
this derivation clearly ensures the thermodynamic consistency of the whole model. Of special interest are the thermodynamic restrictions affecting the drift–diffusion boundary conditions, Eqs. (21)–(23), for they must be satisfied for any proposed boundary condition.

As in any phenomenological model, explicit expressions for some functions or parameters are not given by the theory itself. Only when the model is applied to several different systems, or when the appropriate microscopic models are proposed, information about these unspecified parts may be obtained. It should be pointed out that, in any case, these results must satisfy the general restrictions imposed by the thermodynamic derivation.

We have shown, in the particular case of unipolar systems, that the model is complete, in the sense that once the physical conditions at infinity are specified, it completely characterises the system. A similar derivation can be developed for bipolar systems.

As a simple application, we have analysed the thermionic emission–diffusion theory for one-dimensional abrupt M–S junctions without interface states and have shown that this theory is thermodynamically consistent, in the sense of the present paper, by showing that it fits well into the framework of the present model. In addition, we have also justified with this example the use of non-linear constitutive relations in the formulation of the discontinuity relations. Similar procedures can be applied to more complicated situations, allowing one to extract very useful information on the semiconductor systems.

Finally, it should be noted that the drift–diffusion model presented here may be generalised in a more or less systematic way, by including other irreversible processes or by considering three-dimensional systems, which would allow us to study, for instance, inhomogeneous junctions [15,16]. Among these generalisations, it is especially important to include recombination–generation processes or tunnelling processes in the model because their relevance to semiconductor devices is well known. The treatment of recombination–generation processes in the framework of non-equilibrium thermodynamics will be considered in future papers. On the other hand, the non-local nature of the tunnelling processes makes their implementation in this (local) framework rather complicated, although some local macroscopic formulations are present in the current literature [18,19].

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Appendix A. On non-equilibrium thermodynamics of systems with interfaces

Our purpose in this appendix is to establish the non-equilibrium thermodynamics basis of multicomponent electrically conducting polarizable systems divided by an interface by following the procedure indicated in [9]. Crucial in this analysis is the derivation of the surface and bulk entropy productions accounting for the irreversible processes occurring in the system. The phenomenological equations derived from these quantities correspond to the constitutive equations for the interfacial and bulk currents and to the boundary conditions.

First of all, we will indicate the way to derive balance equations at interfaces [7]. To this purpose, let us focus on an unspecified quantity \( d \) defined in the whole system. Its evolution is directed by the balance equation

\[
\frac{\partial}{\partial t} d_V + \text{div} \, J_d = \sigma_d , \tag{A.1}
\]

where \( J_d \) and \( \sigma_d \) are the corresponding current and production, and where the subindex \( V \) means that this density is per unit of volume. Now, using the decomposition of the fields in terms of the bulk fields and excess fields given through Eq. (1) we arrive at

\[
\left( \frac{\partial}{\partial t} d_V^+ + \text{div} \, J_d^+ - \sigma_d^+ \right) \theta^+ + \left( \frac{\partial}{\partial t} d_V^- + \text{div} \, J_d^- - \sigma_d^- \right) \theta^- \\
+ \left( \frac{\partial}{\partial t} d_{ex} + \text{div} \, J_{d,ex} + \hat{n} \cdot [J_d] - \delta^+ - \sigma_{d,ex} \right) = 0 , \tag{A.2}
\]

where \( \delta^+ \) is Dirac’s delta function coming from the derivatives of Heaviside’s functions [7], \( \hat{n} \) is the unit normal vector pointing from \(-\) \to \(+\) and \([A]_- = A^+(0, y, z) - A^-(0, y, z)\) (we are assuming that the interface is at rest and is identified with the plane \( x = 0 \)). In the bulk, \( d^\pm \) obeys the balance equations

\[
\frac{\partial}{\partial t} d_V^\pm + \text{div} \, J_d^\pm = \sigma_d^\pm . \tag{A.3}
\]

As a consequence, the two first lines in Eq. (A.2) vanish. By averaging the remaining third term as well as using the definition of the surface fields given in Eq. (2) we arrive at the surface balance equation

\[
\frac{\partial}{\partial t} d_A + \text{div} \, J_{d,\parallel} + \hat{n} \cdot [J_d]_- = \sigma_d^s . \tag{A.4}
\]

where the subindex \( A \) refers to the fact that the density is per unit of area, and where only the parallel component of the current appears because the integration of the normal component vanishes. Usually, one defines a surface flux with no normal component and calls this restriction a transversality condition. Further details may be seen in Ref. [7].
We will now apply the former scheme in order to obtain the set of balance equations describing the evolution of the relevant quantities in the system. For the balance of mass of the $k$th component one has

$$\frac{\partial}{\partial t} \rho_k^\pm + \text{div} \ J_{k,\pm} = \sigma_k^\pm, \quad k = 1, 2, 3, \quad (A.5)$$

$$\frac{\partial}{\partial t} \rho_k^+ + \text{div} \ J_{k,1} + \dot{\mathbf{n}} \cdot [J_k]_- = \sigma_k^+, \quad k = 1, 2, 3, \quad (A.6)$$

where $J_{k,\pm}$ and $J_{k,1}$ are the diffusion currents and $\sigma_k^\pm$ and $\sigma_k^+$ the production rates. From these equations one may derive the balance equations for the total mass $\rho^\pm = \sum_{k=1}^3 \rho_k^\pm$, $\rho^+ = \sum_{k=1}^3 \rho_k^+$ and total charge, $q_v^\pm = \sum_{k=1}^3 z_k \rho_k^\pm$, $q_A^+ = \sum_{k=1}^3 z_k \rho_k^+$, with $z_k$ being the charge-mass ratio of the $k$th component,

$$\frac{\partial}{\partial t} \rho_v^\pm + \text{div} \ J_{\rho,\pm} = 0, \quad (A.7)$$

$$\frac{\partial}{\partial t} \rho^+ + \text{div} \ J_{\rho,1} + \dot{\mathbf{n}} \cdot [J_{\rho}]_- = 0, \quad (A.8)$$

$$\frac{\partial}{\partial t} q_v^\pm + \text{div} \ J_{c,\pm} = 0, \quad (A.9)$$

$$\frac{\partial}{\partial t} q_A^+ + \text{div} \ J_{c,1} + \dot{\mathbf{n}} \cdot [J]_- = 0, \quad (A.10)$$

where we have taken into account the reaction conservation relations $\sum_{k=1}^3 \sigma_k^\pm = 0$, $\sum_{k=1}^3 z_k \sigma_k^\pm = 0$, $\sum_{k=1}^3 \sigma_k^+ = 0$, $\sum_{k=1}^3 z_k \sigma_k^+ = 0$, and we have defined the total mass currents as $J_{\rho,\pm} = \sum_{k=1}^3 J_{k,\pm}$, $J_{\rho,1} = \sum_{k=1}^3 J_{k,1}$ and the charge conducting currents as $J_{c,\pm} = \sum_{k=1}^3 z_k J_{k,\pm}$, $J_{c,1} = \sum_{k=1}^3 z_k J_{k,1}$.

In the same way for the balance of momentum one has

$$\frac{\partial}{\partial t} \mathbf{g}_v^\pm + \text{div} \ \mathbf{P}^\pm = \mathbf{f}_v^\pm, \quad (A.11)$$

$$\frac{\partial}{\partial t} \mathbf{g}_A^+ + \text{div} \ \mathbf{P}^+ + \dot{\mathbf{n}} \cdot [\mathbf{P}]_- = \mathbf{f}_A^+, \quad (A.12)$$

where $\mathbf{g}_v^\pm$ and $\mathbf{g}_A^+$ are the momentum densities, $\mathbf{P}^\pm$ and $\mathbf{P}^+$, the pressure tensors and $\mathbf{f}_v^\pm$ and $\mathbf{f}_A^+$ the density force fields. Precise expressions for these quantities can be found in Ref. [4] for the bulk and in Ref. [9] for the interface.

Finally, the balance for the total energy is given by

$$\frac{\partial}{\partial t} e_v^\pm + \text{div} \ J_e^\pm = 0, \quad (A.13)$$

$$\frac{\partial}{\partial t} e_A^+ + \text{div} \ J_e^+ + \dot{\mathbf{n}} \cdot [J_e]_- = 0, \quad (A.14)$$
where $J^+ \vec{v}$ and $J^- \vec{v}$ are the energy currents. The internal energy equations follow from the previous equations provided the total energy is expressed in terms of the internal energy and kinetic and potential contributions. One then arrives at

$$\frac{\partial}{\partial t} u^+ _v + \text{div} J^+ _u = \sigma^+_u,$$

(A.15)

$$\frac{\partial}{\partial t} u^- _A + \text{div} J^- _u + \hat{n} \cdot [J_u]_+ = \sigma^- _u,$$

(A.16)

where $J^+ _u$ and $J^- _u$ are the internal energy current and $\sigma^+_u$ and $\sigma^- _u$ are the internal energy productions (see Refs. [4,9] for explicit expressions of these quantities).

In order for the system of balance equations to become a complete set of differential equations for the fields, we need explicit expressions for the currents appearing in them. These can be obtained in the framework of non-equilibrium thermodynamics.

In fact, after assuming local equilibrium, we then propose the fundamental equations in the bulks and at the surface,

$$ s^+_v = f^+ (u^+_v, \rho_z ^+ , P^+_v, M^+_v), $$

(A.17)

$$ s^- _A = f^- (u^- _A, \rho_z ^- , P^- _A, M^- _A) $$

(A.18)

(or Gibbs equations when they are expressed in differential form), to hold locally. After derivation with respect to time, one then obtains the following equations in the bulks:

$$ \frac{\partial}{\partial t} s^+_v = \frac{1}{T^+} \frac{\partial}{\partial t} u^+_v - \sum_{k=1}^{3} \mu^+_k \frac{\partial}{\partial t} \rho^+_k - \frac{E^+_eq}{T^+} \frac{\partial}{\partial t} P^+_v + \frac{B^+_eq}{T^+} \frac{\partial}{\partial t} M^+_v \quad \text{and at the interface} \quad \frac{\partial}{\partial t} s^- _A = \frac{1}{T^-} \frac{\partial}{\partial t} u^- _A - \sum_{k=1}^{3} \mu^- _k \frac{\partial}{\partial t} \rho^- _k - \frac{A^+_1eq}{T^-} \frac{\partial}{\partial t} P^- _A - \frac{A^+_2eq}{T^-} \frac{\partial}{\partial t} M^- _A. $$

(A.19)

In (A.19) the primes refer to the bulk baricentric velocity and in (A.20) to the surface baricentric one. Moreover, the thermodynamic definitions of the intensive parameters have been used.

Following Ref. [9] we will take

$$ A^1 _1 = ([D_n]_+ , [E_n]_+), $$

(A.21)

$$ A^2 _2 = ([B_n]_+ , [H_n]_+) $$

(A.22)

as the conjugate variables of the surface polarisations. Then, by inserting the expressions for the balance equations previously stated in Eqs. (A.19) and (A.20), one arrives at the expressions for the bulk and surface entropy balance equations:

$$ \frac{\partial}{\partial t} s^+_v + \text{div} J^+_v = \sigma^+_v $$

(A.23)

$$ \frac{\partial}{\partial t} s^- _A + \text{div} J^- _u + \hat{n} \cdot [J_u]_+ = \sigma^- _u $$

(A.24)
where \( J^\pm_s \) and \( J^\pm_r \) are the entropy currents and \( \sigma^\pm_s \) and \( \sigma^\pm_r \) are the bulk and surface entropy productions. The explicit calculations for \( J^\pm_s \) and \( J^\pm_r \), and \( \sigma^\pm_s \) and \( \sigma^\pm_r \) may be found in Refs. [4,9]. For the drift–diffusion model we are considering, which in particular neglects relaxation polarisation phenomena, generation–recombination processes, thermal, magnetic and viscous effects, one then obtains [4]

\[
\sigma^\pm_s = -\frac{1}{T} \sum_{k=1}^{3} J^\pm_k \cdot (\text{grad } \mu^\pm_k - z_k E^\pm)
\]

(A.25)

and

\[
J^\pm_{s,r} = \frac{1}{T} \left( J^\pm_{d,r} - \sum_{k=1}^{3} \mu^\pm_k J^\pm_k \right),
\]

(A.26)

where the primed fluxes are defined as \( J^\pm_{d,r} = J^\pm_d - v^\pm d^\pm \). Here \( v^\pm \) is the baricentric velocity defined through \( \rho^\pm v^\pm = J^\pm_p \). For a one-dimensional system, Eq. (A.25) is precisely Eq. (27) used in Section 3.2.

A similar, but much more complicated, analysis provides the expressions for the surface flux and entropy production [9]. For a one-dimensional system no equation for the flux is necessary. For the entropy production, in the drift–diffusion approximation, one obtains [9],

\[
\sigma^s = -\frac{1}{T_s} \sum_{k=1}^{2} [J_k (\mu_k - \mu^s_k)]_+ + \frac{1}{T} E^s_\nu \left[ \sum_{k=1}^{2} z_k J_k \right]_+
\]

(A.27)

where terms proportional to the third power of velocity have been neglected, and where \( E^s_\nu \) is the surface variable corresponding to the normal component of the electric field. In this paper, we have assumed that the surface is not polarizable, that is \( P^s_{4,n} = 0 \). Due to the relation, see Ref. [9], \( P^s_{4,n} = -E^s_\nu \), one then has \( E^s_\nu = 0 \). In this case, Eq. (A.27) transforms into Eq. (33) used in Section 3.2. In some cases it is useful to take into account the surface polarisation [20]. In these cases, one can show that the discontinuity in the electric potential is given by \( [V]_+ = -E^s_\nu \), and that one needs an additional surface state equation, that can be written, for instance as \( P^s_{4,n} = P^s_{4,n}([D]_+) \). It is worth noting that even in this case Eq. (A.27) can be rewritten as Eq. (36).

References