Non-equilibrium thermodynamics of thermionic emission processes in abrupt semiconductor junctions, including the effects of surface states

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Abstract

The methods of non-equilibrium thermodynamics of systems with an interface have been applied to the study of thermionic emission processes in abrupt semiconductor junctions, including the effects of surface states. Our analysis covers different situations of interest, concerning unipolar and bipolar systems, either degenerate or not, with or without interface states and under steady and non-steady conditions. In this way, a complete phenomenological modelling of thermionic emission-interface states processes has been proposed, overcoming some of the inherent limitations of the currently existing models.
I. INTRODUCTION

Metal-semiconductor contacts have been extensively studied in the literature [1], [2]. At the beginning, basically two different approaches were followed to describe their rectifying properties: the diffusion approach [3], in which the main current limiting mechanism was the diffusion of carriers through the semiconductor; and the thermionic emission (TE) approach [4], in which the dominant process was the thermal emission of carriers over the contact barrier. These two approaches were synthesized later [5], giving rise to the so-called thermionic emission-diffusion (TE-D) models, in which both current limiting processes were taken into account. A similar development occurred in the more recent area of heterojunctions, in which both TE [6], and TE-D [7] models were also proposed.

These models have been further generalised by including the effects of interface states that very often are present at semiconductor junctions, see for instance, [8], [9], [10]. One may call these generalizations thermionic emission-interface state-diffusion (TE-IS-D) models. In some cases, mostly in the context of metal-semiconductor (MS) junctions, a thin insulating layer was introduced to account for some non-ideal properties [1], [2]. Its main effect was to allow the electric potential to be discontinuous across the junction. Therefore, in this paper we will distinguish between abrupt junctions (continuous electric potential) and non-abrupt ones (discontinuous electric potential). For many purposes, the models mentioned above suffice to describe most of the properties of semiconductor junctions [3], [10].

Despite their wide application, a general phenomenological derivation of those models is still lacking in the current literature. This may be due to the fact that the TE-IS and diffusion processes are, a priori, of a different nature, which suggests applying to the former a microscopic-kinetic approach, while to the latter a phenomenological one. As a consequence, this fact has caused a situation where the models are not formulated in a general enough way, in the sense that some situations or processes have not been explored, mainly those with respect to the TE-IS processes.
It is our purpose in this paper to present a complete analysis of the TE-IS processes in abrupt semiconductor junctions. This study overcomes some of the inherent limitations of the previous models and provides a proper framework to study these junctions in a more complete way.

We would like to draw special attention to the fact that we will develop the whole analysis in the same phenomenological framework as where diffusion processes may be treated, allowing us then to present a unified derivation of the TE-IS-D models in abrupt semiconductor junctions. In this way all the situations and processes may be studied, including the effects of degenerancy, bipolarity, non-stationarity or interface state filling, which are treated only in an approximate way in most of the models mentioned above.

The organisation of the paper is as follows: In section II, we summarize the main results concerning non-equilibrium thermodynamic description of semiconductor junctions. In this framework, and with the help of the formalism of the internal degrees of freedom, we derive in section III the TE law for abrupt unipolar junctions without interface states. This result is further generalised in section IV, to include the effects of interface states or bipolarity. Finally, in section V we summarize our main results.

II. NON-EQUILIBRIUM THERMODYNAMIC DESCRIPTION OF SEMICONDUCTOR JUNCTIONS

When two different semiconductors (or, in general, two different materials) are in contact, a very narrow region exists in between, which exhibits peculiar macroscopic behaviour. It has been shown that the properties of this region can be explained in a simple way, by substituting it by a two-dimensional interface, with its own macroscopic properties, and by assuming that the bulks to will behave as in the absence of the junction just up to this interface. This introduces a discontinuous description of the system, in which the relevant fields are the extrapolated bulk fields (discontinuous through the interface) and the surface fields (to describe surface properties). The discontinuity in the bulk fields makes it
necessary to introduce some discontinuity relationships in the description of these systems, and the presence of the two-dimensional interface the proper surface equations to describe its properties. A systematic and thermodynamically consistent way to derive a complete set of equations (bulk, interface and discontinuity equations) to describe these systems, is provided by the theory of non-equilibrium thermodynamics of systems with interfaces [16, 18]. Precisely, by following this approach, a one dimensional phenomenological model for drift-diffusion processes in abrupt semiconductor junctions was derived in [11], which included, apart from the usual drift-diffusion bulk equations, the corresponding surface and discontinuity relations.

Of particular interest for the present paper are the discontinuity relationships for the drift-diffusion processes, for they describe the TE-IS processes that take place at the semiconductor junction. To arrive at these discontinuity relations, we first evaluated in [11] the surface entropy production corresponding to a semiconductor junction when only drift and diffusion processes are considered. For a one-dimensional system one obtains [11],

$$\sigma^s = -\frac{1}{T} \vec{J}^+ \cdot \vec{X}^+ - \frac{1}{T} \vec{J}^- \cdot \vec{X}^-$$  \hspace{1cm} (1)

for the case in which interface states are present, and

$$\sigma^s = -\frac{1}{T} \vec{J}^+ \cdot [\vec{\phi}]_-$$  \hspace{1cm} (2)

when they are not. In Eqs. (1) and (2), we have defined $\vec{J}^\pm = (J_1^\pm, J_2^\pm)$, where $J_k^\pm$ stands for the perpendicular component to the interface of the current density number of electrons (k=1) and holes (k=2), evaluated at the left (−) and right (+) hand sides of the junction. Similarly, we have $\vec{X}^\pm = (X_1^\pm, X_2^\pm)$, $[\vec{\phi}]_- = ([\phi_1]_-, [\phi_2]_-)$, with $X_k^+ = \phi_k^+ - \phi_k^s$, $X_k^- = \phi_k^s - \phi_k^-$, and $[\phi]_- = \phi_k^+ - \phi_k^-$, with $\phi_k^{\pm,s}$ being the corresponding electrochemical potentials (quasi-Fermi levels) for the k-th carrier in the bulks (±), or at the interface (s), defined as

$$\phi_k^+ = \mu_k^+ + q_k V^\pm, \quad \phi_k^s = \mu_k^s + q_k [V]_+; \quad k = 1, 2$$  \hspace{1cm} (3)

where $\mu_k^{\pm,s}$ are the chemical potentials (Fermi levels), $q_k$ the charge of the k-th carrier, and $V^\pm$ the electric potential with $[V]_+ = \frac{1}{2}(V^+ + V^-)$. All the magnitudes defined above are
evaluated at the interface, that is, at \( x = 0 \). For abrupt junctions, the electric potential is continuous across the junction, then one has \([V] = 0\).

From these entropy productions the following discontinuity relations may be derived [11],

\[
\vec{J}^\pm = -\frac{1}{T} \vec{F}^\pm (\vec{X}^+, \vec{X}^-)
\]

which is valid when interface states are present. Otherwise, the corresponding relation is

\[
\vec{J}^+ = -\frac{1}{T} \vec{F}(\vec{\phi}^-)
\]

In the above equations, \( \vec{F}^\pm \) and \( \vec{F} \) are some unspecified functions satisfying the equilibrium condition

\[
\vec{F}^\pm (\vec{0}, \vec{0}) = \vec{F}(\vec{0}) = 0
\]

the second principle of thermodynamics

\[
\vec{X}^+ \cdot \vec{F}^+ + \vec{X}^- \cdot \vec{F}^- \geq 0
\]

\[
[\vec{\phi}]^- \cdot \vec{F} \geq 0
\]

and the Onsager’s symmetry relations

\[
\frac{\partial F_\alpha^k}{\partial X_j^\beta} \bigg|_{eq} = \frac{\partial F_j^\beta}{\partial X_k^\alpha} \bigg|_{eq} \quad k, j = 1, 2 \quad \alpha, \beta = +, -
\]

\[
\frac{\partial F_1}{\partial [\phi_2]} \bigg|_{eq} = \frac{\partial F_2}{\partial [\phi_1]} \bigg|_{eq}
\]

Finally, it should be noted that the functions \( \vec{F}^\pm \) (\( \vec{F} \)) may also depend on the bulk number densities, \( n_k^\pm \) (surface number density \( n_k^s \)) and on temperature, \( T \) [11].

For the case under consideration, in which recombination-generation or tunnelling processes are neglected, one usually assumes that the transport of current across the interface is controlled by the thermal excitation of carriers over the barrier (or barriers) that appears at the junction. For this reason, we will call Eqs. (4) and (5) the TE-IS and TE relations, respectively and the search for explicit expressions for them is the main purpose of next sections.
III. THERMIONIC EMISSION RELATION FOR UNIPOLAR ABRUPT JUNCTIONS

As commented previously, the derivation of all these expressions will be carried out by means of the methods of non-equilibrium thermodynamics. Due to the intrinsic non-linear nature of the emission processes, one has to go beyond the usual linear phenomenological relations, and propose more general ones. One way to systematically derive such a non-linear relations, still under the framework of non-equilibrium thermodynamics, is provided by the formalism of the internal degrees of freedom. This will be the approach we will follow in this paper. For the sake of clarity, we will devote the next subsection to introduce the internal degrees of freedom in the context of semiconductor junctions, postponing the derivation of the TE relation for next subsection.

A. Internal degrees of freedom and semiconductor junctions

In the thermodynamic description of a system one has to distinguish between transport and relaxation processes. For the former, transport equations accounting for the evolution of quantities, as density, velocity, etc. can be formulated starting from the conservation laws of mass, momentum, etc. Transport equations then describe the evolution of those quantities, essentially due to two mechanisms namely, diffusion and convection. Relaxation processes involve transformations occurring at each point of the system whose mechanism is intrinsically non-linear and is usually modelled by the pass through a potential barrier. In non-equilibrium thermodynamics language this process may be viewed as diffusion in an internal space, the space of the internal variable. These scheme has been satisfactorily applied to a number of physical situations.

Concerning semiconductor junctions the following example will illustrate the way of introducing internal variables to arrive at a complete characterization of the system. Let us consider the emission of a carrier through the interface. When the carrier reaches the
interface, it has several options: to jump directly into the other side of the junction, or into an empty surface state, or simply to go back. The net effect of these processes is known to be non-linear [11], in the sense that linear expressions for Eqs. (4) or (5), do not correctly describe them. To derive these non-linear relations within the framework of non-equilibrium thermodynamics, one may use the internal variables. In this alternative picture, one may consider that the different processes a carrier may go through when it reaches the interface, are well represented by a continuous diffusion process in the internal space, over an energy barrier which matches the discontinuity points at the interface. The carriers following this continuous process will be called activated carriers, and the coordinate that describes it, the internal coordinate.

By introducing an internal space for each elementary process, whose number may be predicted directly from the expression of the entropy production, the net rate corresponding to them may be evaluated, allowing one to arrive at an explicit expression for Eqs. (4) and (5).

It is worth emphasizing that both pictures (internal degrees of freedom and macroscopic discontinuity) leads to the same entropy production [12], [15], and it is this fact that enables us to use the former to derive explicit non-linear constitutive relations, provided the latter one is unable to.

B. Thermionic emission relation

For the case of unipolar, i.e. those with only a single carrier, abrupt semiconductor junctions without interface states, the surface entropy production may be written as Eq. (2),
\[
\sigma^s_s = -\frac{1}{T} J^+_e [\phi_e]_-
\]

For the sake of definiteness, we have taken the electrons as the single carrier and the corresponding magnitudes have been denoted by the subindex e. This entropy production corresponds to a single elementary process, as can be seen by comparing it with the one corresponding to an unimolecular reaction of the form
\[ e^- \leftrightarrow e^+ \]  

(12)

provided one identifies \( J_e^+ \) with the reaction rate and \( [\phi_e]^- \) with the affinity (see [12], [18]). Furthermore, this equivalence between chemical reactions and emission processes, allows us to directly write the corresponding constitutive relation for the latter case by simply identifying the corresponding magnitudes in the former case. In this way we obtain, in the general case of a degenerate (non-ideal) system, [12], [18],

\[ J_e^+ = k_B l \left( 1 - e^{\beta[\phi_e]^-} \right) \]  

(13)

with

\[ l = \frac{e^{\beta[\phi_e]^-}}{k_B \int_{\gamma_1}^{\gamma_2} D(\gamma)^{-1} e^{\beta U(\gamma)} f(\gamma) \left( 1 + \frac{\partial \ln f}{\partial \ln n} \right) d\gamma} \]  

(14)

where \( k_B \) is Boltzmann’s constant, \( \beta = (k_B T)^{-1} \), \( \gamma \) is the internal coordinate, having values in the interval \([\gamma_1, \gamma_2]\) of the internal space, \( D(\gamma) \) is the diffusion coefficient in the internal space, \( U(\gamma) \) is the internal energy barrier, \( n(\gamma) \) is the density number of activated electrons at point \( \gamma \), and \( f(\gamma) = f(n(\gamma), T) \) accounts for the degenerancy effects, and is defined through the state equation

\[ \phi(\gamma) = k_B T \ln f(\gamma)n(\gamma) + U(\gamma) \]  

(15)

where \( \phi(\gamma) \) is the generalised chemical potential of the activated electrons. For the case of a non-degenerate system, \( f \) is only a function of \( T \), which considerably simplifies Eqs. (14) and (15). In Eqs. (13) and (14) we have used \( \phi(\gamma_1) = \phi_e^- \) and \( \phi(\gamma_2) = \phi_e^+ \), for at these points the internal space makes contact with the external one. Moreover, in what follows, we will also identify \( f(n(\gamma_1), T) = f_e^-(n_e^-, T) \), \( f(n(\gamma_2), T) = f_e^+(n_e^+, T) \) and \( U(\gamma_1) = U_e^- \), \( U(\gamma_2) = U_e^+ \). In the non-degenerate case \( f_e^{\pm, nd} = (N_e^{\pm})^{-1} \), where \( N_e^{\pm} \) is the effective density of states, which is only a function of \( T \). As we have assumed the mass of the carriers to be the same on each side of the junction, we will then have that \( N_{e^-} = N_{e^+} \equiv N_e \).

A simplified expression for Eq. (14) may be obtained by introducing a mobility into the internal space, \( \tilde{\mu} \), through Einstein’s relation
\[
\frac{D(\gamma)}{\tilde{\mu}(\gamma)} = n(\gamma) \frac{\partial (\phi(\gamma) - U(\gamma))}{\partial n(\gamma)} = k_B T \left( 1 + \frac{\partial \ln f}{\partial \ln n} \right). \tag{16}
\]

We then obtain
\[
l = T \frac{e^{\beta \phi_e^+}}{k_B \int_{\gamma_2}^{\gamma_1} \tilde{\mu}(\gamma)^{-1} e^{\beta U(\gamma)} f(\gamma) d\gamma}. \tag{17}
\]

For the purposes of this paper, it is convenient to define a transition coefficient as follows
\[
\lambda_{-+} \equiv k_B \frac{l}{f e^{-\phi_e^-}}. \tag{18}
\]

With this definition, and by substituting Eq. (17) in it, we have
\[
\lambda_{-+} = T \frac{1}{\int_{\gamma_2}^{\gamma_1} \tilde{\mu}(\gamma)^{-1} e^{\beta (U(\gamma) - U(\gamma_1))} f(\gamma) d\gamma}. \tag{19}
\]

Note that for an abrupt junction, \( U(\gamma) \) is a given function independent on the density number. Moreover \( \tilde{\mu} \) may also be considered independent of the density number, even for a degenerate system. Hence, the main dependence of \( \lambda_{-+} \) on the density is given through \( f \). As a consequence, for a non-degenerate system, in which \( f \) is only a function of \( T \), this transition coefficient will be independent on the densities.

Similarly, we may define the inverse transition coefficient, \( \lambda_{+-} \), as
\[
\lambda_{+-} \equiv \lambda_{-+} e^{\beta \Delta U} \tag{20}
\]
where \( \Delta U = U(\gamma_2) - U(\gamma_1) = U_e^+ - U_e^- \) represents the discontinuity in the electron energy, which for an abrupt junction is independent of the density.

By using this coefficient we may rewrite Eq. (13) as
\[
J_e^+ = \lambda_{+-} e^{-e^{\beta \phi_e^+}} \left( 1 - e^{\beta \phi_e^-} \right) \tag{21}
\]
where \( e^{\phi_e^+} = U_e^+ - \phi_e^- \). It is easily seen that Eq. (21), or alternatively Eq. (13), satisfy the unipolar version of the thermodynamic requirements presented in section II, Eqs. (6) and (8) (no symmetry relation is needed here). Moreover, as predicted in that case, the discontinuity relation only depends on the thermodynamic force, in this case \( [\phi_e]^- \), and on...
$n_e^{\pm}$, through $\lambda_{+-}$, and $T$. On the other hand, for the non-degenerate case, $\lambda_{+-}$, is only a function of $T$, and we denote it by $\lambda_{nd}^{+-}$.

Let us show that Eq. (13), in the non-degenerate case, is precisely equivalent to the boundary conditions used in the TE-D theories [1]. By simply noting that for that case one has

$$n_e^{\pm} = N_e^e e^{\beta (\varphi_e^{\pm} - U_e^{\pm})} \quad (22)$$

we can rewrite Eq. (21) as

$$eJ_e^+ = e \frac{\lambda_{nd}^{+-}}{N_e^e} (n_m^+ - n_e^+) \quad (23)$$

where $n_m^+ = N_e e^{-\beta \varphi_e^+}$. If we identify $v_R \equiv \frac{\lambda_{nd}^{+-}}{N_e^e}$, we then see that Eq. (23) is precisely the boundary condition used in [1], in the context of MS junctions. A kinetic calculation for it gives [1] $v_R = \frac{A^* T^2}{eN_e}$, with $A^*$ being Anderson’s modified constant. Therefore, we obtain $\lambda_{nd}^{+-} = \frac{A^* T^2}{e}$, which is, as mentioned above, only a function of $T$.

Moreover, by using Eq. (22) again, we may rewrite Eq. (21) as

$$eJ_e^+ = e \frac{\lambda_{nd}^{+-}}{N_e^e} (n_e^+ e^{-\beta \Delta U} - n_e^+) \quad (24)$$

which corresponds to the boundary condition proposed in [7] in the context of heterojunctions. It is worth pointing out that Eqs. (23) and (24) reduce, respectively, to Bethe’s [4] and Anderson’s [6] expressions, in the limit in which diffusion processes are neglected.

IV. THERMIIONIC EMISSION-INTERFACE STATE RELATIONS FOR ABRUPT SEMICONDUCTOR JUNCTIONS

Our aim in this section is to generalise the results of the previous section, by including the effects of interfacial states or by considering bipolar systems, i.e. systems with two types of carriers.
A. Unipolar systems with interfacial states

For this case the surface entropy production can be written as, see Eq. (1),

\[
\sigma_s^* = -\frac{1}{T} J_e^+ X_e^+ - \frac{1}{T} J_e^- X_e^- = \frac{1}{T} J_e^- (\phi_e^- - \phi_e^+) - \frac{1}{T} (-J_e^-) (\phi_e^- - \phi_e^+).
\]

(25)

This expression is reminiscent of the entropy production corresponding to the set of independent elementary processes concerning the interchange of electrons among bulks and surface,

\[
\begin{align*}
e^- & \rightleftharpoons e^s \\
e^s & \rightleftharpoons e^+ \\
e^- & \rightleftharpoons e^+
\end{align*}
\]

(26)

labelled by \(\alpha = 1, 2, 3\), with reaction rates \(J_1 = -J_e^-\), \(J_2 = J_e^+ - J_e^-\), \(J_3 = J_e^+\), and conjugated affinities \(A_1 = X_e^-\), \(A_2 = X_e^+\), \(A_3 = X_e^- + X_e^+ = [\phi_e^-]_\cdot\)

The equivalence with the chemical reaction case analyzed in [12], allows us to directly formulate the constitutive relations

\[
J_i = \sum_{\alpha=1}^{3} k_B \nu_{i\alpha} l_\alpha \left( 1 - e^{\beta A_\alpha} \right) \quad i = 1, 2, 3
\]

(27)

where \(\nu_{i\alpha}\) is the stoichiometric coefficient of the \(i\)-th electron (we identify \(e^- \equiv e_1\), \(e^s \equiv e_2\) and \(e^+ \equiv e_3\) ) participating in the \(\alpha\)-th elementary reaction, \(A_\alpha\) are the affinities defined above and

\[
l_\alpha = \frac{e^{\beta \phi_\alpha(\gamma_\alpha)}}{k_B \int_{\gamma_{\alpha_1}}^{\gamma_{\alpha_2}} D_\alpha(\gamma_\alpha)^{-1} e^{\beta U_\alpha(\gamma_\alpha)} f_\alpha(\gamma_\alpha) \left( 1 + \frac{\partial \ln f_\alpha}{\partial \ln \gamma_\alpha} \right) d\gamma_\alpha}
\]

(28)

where \(\phi_\alpha(\gamma_\alpha)\) corresponds to the generalised chemical potential of the reactant in the \(\alpha-th\) reaction. As before, by introducing a mobility, \(\bar{\mu}_\alpha\), through Einstein’s relation we can rewrite Eq. (28) as

\[
l_\alpha = T \frac{e^{\beta \phi_\alpha(\gamma_\alpha)}}{\int_{\gamma_{\alpha_1}}^{\gamma_{\alpha_2}} \bar{\mu}_\alpha(\gamma_\alpha)^{-1} e^{\beta U_\alpha(\gamma_\alpha)} f_\alpha(\gamma_\alpha) d\gamma_\alpha},
\]

(29)
For the elementary processes under consideration, Eq. (26), we have

\[
(\nu_{i\alpha}) = \begin{pmatrix}
-1 & 1 & 0 \\
0 & -1 & 1 \\
1 & 0 & -1
\end{pmatrix}.
\] (30)

By substituting these values into Eq. (27), we obtain the following constitutive relations,

\[
J^+_e = k_B \left[ l_2 \left( 1 - e^{\beta X^+_e} \right) + l_3 \left( 1 - e^{\beta [\phi_e]^-} \right) \right]
\] (31)
\[
J^-_e = k_B \left[ l_1 \left( 1 - e^{\beta X^-_e} \right) + l_3 \left( 1 - e^{\beta [\phi_e]^-} \right) \right].
\] (32)

Note that the right hand sides of the previous equations are actually functions of the thermodynamic forces, \(X^+_e, [\phi_e]^-\) (only two of them are independent because \([\phi_e]^- = X^+_e + X^-_e\), and of \(T\) and \(n^e_s\). To see this last dependence, we note that although the phenomenological coefficients, at first sight, may also depend on the bulk densities, \(n^e_\pm\), this dependence gives rise to a dependence on \(n^e_s\) and \(X^\pm_e\), through the equations of state

\[
f^\pm_e n^\pm_e = e^{\beta (U^\pm_e - U^e_s)} e^{\pm \beta X^\pm_e} f^s n^s_e.
\] (33)

Furthermore, by construction, Eqs. (31) and (32) satisfy the thermodynamic restrictions given through Eqs. (6), (7) and (9). We therefore conclude that they constitute acceptable thermodynamic constitutive relations.

As in section III, a more useful form of these constitutive relations is obtained by defining the following transition coefficients

\[
\lambda_{ij} \equiv - \sum_{\alpha=1}^{\alpha=3} \nu_{i\alpha} l_{\alpha} V_{j\alpha} \frac{z_i}{z_i}, \quad i < j
\] (34)
\[
\lambda_{ij} \equiv \lambda_{ji} e^{\beta \Delta U_{ij}} \quad , \quad i > j
\] (35)

where \(z_i = f_i n_i\) are the activities and \(\Delta U_{ij} = U_i - U_j\). We then obtain a master-like equation

\[
J_i = \sum_{j=1}^{j=3} \lambda_{ij} z_j - \sum_{j=1}^{j=3} \lambda_{ij} z_i \quad , \quad i = 1, 2, 3 \quad ; \quad i \neq j.
\] (36)

Note that for an abrupt junction \(\Delta U_{ij}\) are given quantities, which allow us to write Eq. (35) as a detailed balance -like expression, \(\lambda_{ij} z^eq_i = \lambda_{ji} z^eq_j\), where we have used \(e^{\beta \Delta U_{ij}} = e^{\beta \Delta U^eq_{ij}} = \frac{z^eq_i}{z^eq_j} \frac{z^eq_j}{z^eq_i} \).
It should be pointed out that in the degenerate case, as can be seen from Eqs. (34) and (35), the transition coefficient may depend on the density number, and hence on the applied bias. On the other hand, in the non-degenerate case, \( f_n \) becomes independent on the density, and then the transition coefficients are only a function of \( T \). In this case, we introduce new transition coefficients \( \lambda_{ij}^0 = \lambda_{ij}^{nd} J_i^{nd} \), where as before we assume \( f_i^{nd} \) to be independent on \( i \) and equal to \( N_e \). Then the constitutive relations transform into \[ J_i = \sum_{j=1}^{3} \lambda_{ji}^0 n_j - \sum_{j=1}^{3} \lambda_{ij}^0 n_i \quad i = 1, 2, 3 ; \quad i \neq j \] (37)

with \( \lambda_{ij}^0 n_i^{eq} = \lambda_{ji}^0 n_j^{eq} \) and \( \lambda_{ij}^0 \) only varying with \( T \).

Keeping these definitions in mind, we may rewrite Eqs. (31) and (32) as
\[ J_e^+ = N_e \lambda_{31}^0 e^{-\beta (U_e^+ - \phi_e^-)} \left( 1 - e^{\beta \phi_e^-} \right) + N_e \lambda_{32}^0 e^{-\beta (U_e^+ - \phi_e^-)} \left( 1 - e^{\beta \phi_e^-} \right) \] (38)
\[ J_e^- = N_e \lambda_{21}^0 e^{-\beta (U_e^- - \phi_e^+)} \left( 1 - e^{\beta \phi_e^+} \right) + N_e \lambda_{31}^0 e^{-\beta (U_e^- - \phi_e^+)} \left( 1 - e^{\beta \phi_e^+} \right) \] (39)

which constitutes the generalization of Eq. (21), or
\[ J_e^+ = \lambda_{31}^0 \left( n_e^- e^{-\beta (U_e^+ - U_e^-)} - n_e^+ \right) + \lambda_{32}^0 \left( n_e^+ e^{-\beta (U_e^+ - U_e^-)} - n_e^- \right) \] (40)
\[ J_e^- = \lambda_{21}^0 \left( n_e^- e^{-\beta (U_e^- - U_e^+)} - n_e^+ \right) + \lambda_{31}^0 \left( n_e^+ e^{-\beta (U_e^- - U_e^+)} - n_e^- \right) \] (41)

which also generalizes Eq. (24). The corresponding expressions valid for the degenerate case may be obtained by simply substituting \( \lambda_{ij}^0 N_e \) by \( \lambda_{ij} \) and \( n_i \) by \( z_i \). This simple rule then justifies the fact that in what follows only the non-degenerate expressions will be treated explicitly.

Some final remarks are in order. First of all, it is worth noting that Eqs. (38) and (39), or alternatively, Eqs. (40) and (41), hold under non-steady conditions for which \( J_e^+ \neq J_e^- \). Moreover, they also include all the possible transitions among interface states and bulks and all the situations of interest (degenerate and non-degenerate systems). Finally, it is worth noting that the number of parameters to be specified is relatively small: the transition coefficients \( \lambda_{21}^0, \lambda_{31}^0, \lambda_{32}^0 \), and the energy discontinuities \( U_e^+ - U_e^-, U_e^- - U_e^+ \) (clearly \( U_e^- - U_e^+ \) is not an independent quantity). This makes the modelling of these processes not as difficult as it would seem a priori.
B. Steady-state conditions

Under steady state conditions Eqs. (38) - (41) can be simplified considerably. In this case one has that $J_e^+ = J_e^-$, see [11], and we then obtain

$$J_e^+ = Ne \left( \lambda_{31}^0 + \frac{1}{(\lambda_{32}^0)^{-1} + (\lambda_{21}^0)^{-1} e^{-\beta(U_e^+ - U_e^-)}} \right) e^{-\beta(U_e^+ - \phi_e^-)} (1 - e^{\beta[\phi_e^-]_-})$$

(42)

$$e^{\beta X_e^+} = \frac{1 + \lambda_{31}^0 e^{\beta(U_e^+ - U_e^-)}}{1 + \lambda_{32}^0 e^{\beta(U_e^+ - U_e^-)} e^{-\beta[\phi_e^-]_-}}$$

(43)

where, as noted in [11], the relevant variable under steady state conditions is $[\phi_e^-]_-$. Alternatively, we can also write

$$J_e^+ = \left( \lambda_{31}^0 + \frac{1}{(\lambda_{32}^0)^{-1} + (\lambda_{21}^0)^{-1} e^{-\beta(U_e^+ - U_e^-)}} \right) \left( n_e^+ - n_e^- e^{-\beta(U_e^+ - U_e^-)} \right)$$

(44)

$$n_e^s = \frac{1}{\lambda_{21}^0 + \lambda_{32}^0 e^{-\beta(U_e^+ - U_e^-)}} \left( \lambda_{21}^0 e^{-\beta(U_e^+ - U_e^-)} n_e^- + \lambda_{32}^0 n_e^+ \right).$$

(45)

The corresponding expressions for the degenerate case are obtained by using the transformation rule formulated previously.

It is worth mentioning that Eqs. (42) and (44) have a TE-like form, see Eqs (21) and (24), but they differ in the fact that now the prefactor incorporates the effects of the interfacial states. Furthermore, we have obtained the equations governing the population of those states under non-equilibrium conditions, Eqs. (43) or (45), in their general form. From these relations, approximate expressions can be proposed. For instance, let us consider the case, very common in the current literature, in which it is assumed that the interface states are in permanent equilibrium with one of the bulk systems, say system $-$. This situation corresponds to the case in which the transitions $e^s \rightarrow e^+$ are practically inhibited as compared to the $e^s \rightarrow e^-$ transitions. In our formulation this means that

$$\frac{\lambda_{21}^0}{\lambda_{32}^0 e^{-\beta(U_e^+ - U_e^-)}} \gg 1.$$  

(46)

Using this approximation in Eq. (42), and considering moderate values for $[\phi_e^-]_-$, we obtain

$$\phi_e^s \approx \phi_e^-$$

(47)
which is the condition of permanent equilibrium between the interface and the system, and which ultimately justifies the use of the bulk chemical potentials to control the filling of the interface states. Moreover, in this case, the prefactor in Eq. (44) reduces to \( \lambda^0_{31} + \lambda^0_{32} \), which is thought to introduce a small modification with respect to the commonly used TE-like expressions. It should be noted that for high values of \( [\phi_e]_- \) this approximation may not be justified, and non-trivial effects coming from the presence of interface states could appear.

C. Bipolar systems

In this subsection, we will consider the case of bipolar systems. For simplicity’s sake we will start by considering the case in which interface states are not present. In this case the surface entropy production reads, Eq. (2),

\[
\sigma_s = \frac{1}{T} [\phi_h]_h - J^+_h - \frac{1}{T} [\phi_e]_e - J^+_e
\]

where the subindex \( h \) stands for holes and \( e \) for electrons. It is easily seen that the elementary processes corresponding to this situation are simply

\[
e^- \iff e^+
\]

\[
h^- \iff h^+
\]

(49)

Note that these processes are decoupled and hence they can be treated separately, proceeding along the lines indicated in section II. The constitutive relations for this case will then read

\[
J^+_e = N_e \lambda^0_{+e} e^{-\beta(U^+_e - \phi^+_e)} \left( 1 - e^{\beta[\phi_e]} \right) =
\]

\[
\lambda^0_{+e} \left( n^-_e e^{-\beta(U^+_e - \phi^-_e)} - n^+_e \right)
\]

(50)

\[
J^+_h = N_h \lambda^0_{+h} e^{-\beta(U^+_h - \phi^+_h)} \left( 1 - e^{\beta[\phi_h]} \right) =
\]

\[
\lambda^0_{+h} \left( n^-_h e^{-\beta(U^+_h - \phi^-_h)} - n^+_h \right)
\]

(51)

(52)

(53)

where the meaning of the different magnitudes clearly follows from the notation. As before, the degenerate case is obtained by applying the corresponding rule. Again by construction
the corresponding thermodynamic restrictions are satisfied. Note that in this case, we have to specify four parameters, the transition coefficients $\lambda_{+0}^{0-}$, $\lambda_{+0}^{h0}$, and the energy discontinuities $U_{e}^{+} - U_{e}^{-}$, $U_{h}^{+} - U_{h}^{-}$. For bipolar heterojunctions the two carriers are hardly ever considered both together, for usually one of the discontinuities is much larger than the other inhibiting the crossing of the corresponding type of carrier [10]. This fact is obviously recovered from our relations.

The introduction of interfacial states in these systems does not complicate the situation very much, because due to the decoupling that exists between the two types of carriers, they can be treated separately, giving rise to a set of equations like the ones obtained in the previous subsection for each of the carriers.

V. CONCLUSIONS

In this paper we have presented a fully thermodynamic and general treatment of thermionic emission processes in semiconductor junctions. All the situations of interest, namely, for unipolar and bipolar systems, which can be degenerate or not, with or without interface states and under steady and non-steady conditions, have been analysed.

The study has been carried out within the framework of non-equilibrium thermodynamics of systems with interfaces, incorporating the formalism of the internal degrees of freedom in order to obtain explicit expressions for the TE-I relations. This procedure has the advantage of allowing us a complete treatment of semiconductor junctions (bulks, interface and discontinuity relations) in a common framework which ensures by construction the thermodynamic consistency and completeness of the relations derived.

Of special interest has been the derivation of general TE-IS relations to describe non-steady situations in the presence of interface states. From these expressions we have then derived the corresponding relations valid at the steady state, which have been shown to incorporate, in the general case, non-trivial contributions that come from the interface states, which might not be negligible in some circumstances. These interface state contributions
are under investigation for some junctions of interest.

Finally, the implementation of the TE-IS expressions in the drift-diffusion model presented in [11], will provide one of the most general TE-IS-D models that has been proposed for abrupt semiconductor junctions, proving therefore the power of the application of the non-equilibrium thermodynamic methods to semiconductor systems.

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REFERENCES

[1] S.M. Sze, “Physics of Semiconductor Devices”, 2nd ed., (J. Wiley & Sons, New York, 1981).

[2] E.H. Rhoderick and R.H. Williams,

“Metal-Semiconductor Contacts”, 2nd ed., (OSP, New York, 1987).

[3] W. Schottky, Naturwissenschaften, 26, 843, (1938).

[4] H.A. Bethe, MIT Radiat. Lab. Rep., 43-12, (1942).

[5] C.R. Crowell and S.M. Sze, Solid State Electron, 9, 1035, (1966).

[6] R.L. Anderson, Solid State Electron., 5, 341, (1962).

[7] D. V. Morgan and R.H. Williams eds., “Physics and Technology of Heterojunction devices”, (P. Peregrims Ltd., London, 1991).

[8] J. Bardeen, Phys. Rev., 71, 717, (1947).

[9] C.Y. Wu, J. Appl. Phys., 51, 3786, (1980).

[10] A.G. Milnes and D.L. Feucht, “Heterojunctions and Metal-Semiconductor junctions”, (Academic, N.Y., 1972).

[11] G. Gomila, J.M. Rubí (preprint)

[12] I. Pagonabarraga, A. Pérez-Madrid, J.M Rubí, (preprint)

[13] I. Pagonabarraga, J.M Rubí, Physica A, 188, 553, (1992).

[14] A. Pérez-Madrid, J.M. Rubí and P.Mazur, Physica A, 212, 231, (1994).

[15] J. Ross and P. Mazur, J. Chem. Phys., 35, 19, (1961).

[16] D. Bedeaux, A.M. Albano, P.Mazur, Physica A, 82, 438, (1976).

[17] D. Bedeaux, “Non-equilibrium Thermodynamics and Statistical Physics of Surfaces”,
in Advances in Chemical Physics, 64, (1986), 47, I. Prigogine and S.A. Rice eds. (Wiley, New York).

[18] S.R. de Groot and P.Mazur, “Non-equilibrium thermodynamics”, (Dover, New York, 1984).