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# NON-EQUILIBRIUM THERMODYNAMICS FRAMEWORK FOR DISLOCATIONS IN SEMICONDUCTOR CRYSTALS AND SUPERLATTICES *

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Dedicated to Professor Mihail Megan
on the occasion of his 70th anniversary

**Abstract**

In the framework of the extended irreversible thermodynamics with internal variables a model for semiconductor crystals and superlattices with dislocations is proposed in order to study the thermal, electrical and mechanical properties of these materials. In the linear approximation, constitutive equations, rate equations for the heat flux and the internal variables are derived. A new dislocation tensor is defined to describe the geometry of these defect lines, because their relative orientation with respect to the superlattice interfaces is very relevant This implies cumbersone equations, but we focus our attention on their general conceptual features. The obtained results may have relevance for miniaturized semiconductor lasers and optimized thermoelectric devices and in other technological sectors.

## 1 Introduction

The behaviour of dislocations in semiconductor superlattices is one of the frontiers in the so called "dislocation engineering", with practical conse-

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quences in material sciences, because it has a direct influence on mechanical properties (plastic behaviour, strain relaxation), on transport properties (heat transport, electric transport and thermoelectric energy conversion) and in optical properties (LED diodes, semiconductor lasers). Some of the topics are the ability of semiconductor superlattices (composed of alternate layers of semiconductors, for instance $Si/Ge, In_xGa_{1-x}As, In_xAl_{1-x}As$, $GaAs/GaAsP, ...$) to filter block dislocations [1]-[7]. In these kinds of problems, both the geometry of the superlattice as well as that of dislocations are relevant, because the interaction between them depends on the relative orientation of the dislocation lines and the interfaces separating the layers of alternating semiconductors.

An analogous problem could be the behaviour of quantized vortex tangles in superfluid helium II submitted to a heat flux [8]-[10]. In this case, the analogous of a superlattice would be a set of mutually parallel grids immersed in helium II; a heat flux perpendicular to them would generate additional vortices at each grid. A difference between both situations is that quantized vortices only exist in the presence of an external heat flow, whereas dislocations may exist without any external forcing.

In this paper, in the framework of the extended irreversible thermodynamics with internal variables [11]-[18], a model for semiconductor crystals (see [19]-[23] and also [24]-[26]) and superlattices with dislocations, is proposed in order to study the effects of dislocations on the mechanical thermal and thermoelectric properties of these materials. Constitutive equations for these systems, the rate equations for heat flux and the internal variables are derived in linear approximation.

Here, to describe the local structure of dislocation lines, a new dislocation tensor is introduced, whose definition is different from the definition à la Maruszewski (see [27], [28]), used by one of the authors (LR) in [19]-[23]. This tensor accounts for the statistical features of the network of very thin dislocation lines, disturbing the otherwise perfect periodicity of the crystal lattice (see [29]-[32]). The trace of this tensor is the dislocation density $\rho_D$, which is often used as a macroscopic average quantity describing the dislocations, but which provides less information than the full dislocation tensor. In our case, instead, more details on the dislocation orientation are necessary to describe their evolution and their interaction with the superlattices interfaces. Furthermore, superlattices are obviously anisotropic, as the behaviour perpendicular or parallel to the interfaces may be very different. Of course, replacing a scalar variable by a tensorial variable for the dislocation implies a higher formal complexity of the equations, which become much more cumbersone. Anyway, in this paper, devoted to the application of the

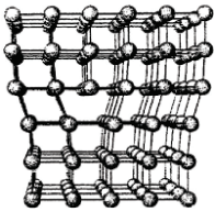

Figure 1: An edge dislocation structure (after [31]).

basic concepts of non-equilibrium thermodynamics, we will focus on general aspects. Semiconductors can present metallurgical defects (for example inclusions, cavities, microfissures, dislocation lines), that sometimes can self propagate because of changed conditions and surrounding conditions that are favorable (see Fig.1). We introduce here the dislocation field and its gradient, related to non-local effects, as internal variables. The dislocations will interact with the lattice of the semiconductor crystal and, very especially, with the interfaces of the superlattice (see Fig.2).

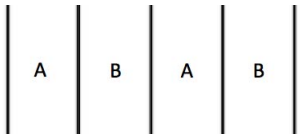


Figure 2: A superlattice of two alternating semiconductors $A$ and $B$. The evolution and the structure of dislocations is influenced by the interfaces.

Understanding the role of internal variables on heat transport is an interesting topic in materials engineering, in order to achieve the most convenient situations for several applications. This topic has two well-defined aspects: a) how the internal variables modify the phonon contribution to the thermal conductivity or the electron and hole contribution to electrical conductivity; b) how the internal variables contribute through their own motion to the heat flux or to mechanical properties, or plastic behaviour.

The effect of dislocations on thermal conductivity and other transport coefficients (electrical conductivity, Seebeck coefficient) has been well studied from the experimental and theoretical points of view [1]-[7]. In fact, the dislocation density $\rho_D$ (total length of dislocation lines per unit volume, which has units of $(\text{length})^{-2}$) has only a minor effect on the thermal conduc-

tivity for dislocation densities smaller than a characteristic value dependent on the material and temperature. For higher values, there is a steep decrease of thermal conductivity. For instance, the critical dislocation density for Si and Ge is of the order of $10^8\ cm^{-2}$. This is due to phonon-dislocation scattering, which is negligible as compared to phonon-phonon scattering (for small dislocation densities $\rho_D$) but which becomes dominant for high values of $\rho_D$.

Furthermore, dislocations reduce electrical conductivity but increase the Seebeck thermoelectric coefficient in some range of dislocation densities ($10^6 cm^{-2} - 10^{10} cm^{-2}$) due to an increase in the entropy of the carriers. Thus, for some ranges of dislocation density the efficiency of thermoelectric energy conversion may be raised by dislocations, especially in low-dimensional structures (films, wires or dots). This makes that dislocation engineering is becoming increasingly useful in the optimization of semiconductor devices [1]-[7].

In Section 2 we introduce the dislocation tensor. In Section 3 we specify the variables and the fundamental laws. In Section 4 we apply the second law of thermodynamics, and in Section 5 we formalize the constitutive theory, with the derivation of constitutive equations and the rate equations for the internal variables and the fluxes.

## 2 The dislocation tensor

First of all, we briefly discusss the mathematical characterization of the dislocation field, by means of a tensor. The dislocation lines disturbe the periodicity of the crystal lattice. They have their intrinsic orientation, which means among other things that dislocations of opposite sign annihilate when the lines critically approach to each other. We consider, as in [27] and [28], a representative elementary sphere volume $\Omega$ of a structure with dislocations, large enough to provide a representation of all the statistical properties of the dislocation lines, that resemble a network of infinitesimally thin channels. In [27] Maruszewski introduces a dislocation core tensor, by treating the dislocation lines as very thin tubes and following a formalism used by Kubik to define a tensor porous [28]. Here, new definitions for the dislocation tensor (different from the definitions in [27]), the polarity vector and the dislocation lines density are given to describe the geometry of these crystal defects, because their relative orientation with respect to the superlattice interfaces is very relevant. An anologous kind of tensor may be used for the description of quantized vortices in turbulent superfluid helium II [8]-[10].

Thus, let us consider an elementary volume of a structure with dislocations. All the microscopic quantities are described with respect to the $\xi_i$ coordinate system ($i = 1, 2, 3$), while macroscopic quantities are described with respect to the $x_i$ axes ($i = 1, 2, 3$). First, by means of the volume averaging procedure, we define the macroscopic scalar variable $\rho_D$ (*dislocation lines density*), representing the average length of dislocation lines per unit volume as

$$\rho_D = \frac{1}{\Omega} \int dl, \tag{1}$$

where $dl$ is the elementary lenght element along the dislocation lines and the integration is worked out over the position $\xi$ along the corresponding dislocation line and over all dislocations present in the chosen integration volume $\Omega$ at $\mathbf{x}$. Also, we define the macroscopic variable, the *polarity vector* $a_i(\mathbf{x})$, that defines the direction and the orientation of dislocations lines by means the average of the microscopic tangent vector $\mathbf{n}(\boldsymbol{\xi})$ along the dislocation lines

$$a_i(\mathbf{x}) = \langle n_i(\boldsymbol{\xi}) \rangle = \frac{1}{\Omega L} \int n_i(\boldsymbol{\xi}) dl, \tag{2}$$

where the integration is carried out over all dislocation lines inside the elementary volume $\Omega$ at $\mathbf{x}$.

Note that $|\mathbf{a}(\mathbf{x})| \in [0, 1]$ measures the directional anisotropy of the tangent to the dislocation lines: in particular $|\mathbf{a}| = 1$ for a totally polarized network of dislocations with all the tangents $\mathbf{n}$ parallel to each other and $|\mathbf{a}| = 0$ for isotropic networks of dislocations. The dislocation field is described by the microscopic tensor

$$\mathbf{a}(\boldsymbol{\xi}) \equiv \mathbf{n} \otimes \mathbf{n}. \tag{3}$$

We define the macroscopic tensor $\mathbf{a}(\mathbf{x})$ as the local average of $\mathbf{a}(\boldsymbol{\xi})$ in the following way

$$a_{ij}(\mathbf{x}) = \langle a_{ij} \rangle = \frac{1}{\Omega} \int_{\Omega} n_i(\boldsymbol{\xi}) n_j(\boldsymbol{\xi}) dl. \tag{4}$$

$a_{ij}$ is called *dislocation tensor* and has unit $m^{-2}$, because it is related to $\frac{dl}{\Omega}$, namely, length/(length)$^3$ =length$^{-2}$. The integration runs along all dislocation lines which are in the chosen integration volume $\Omega$ at $\mathbf{x}$. It models the anisotropy of the network of the dislocation lines inside $\Omega$. The tensor $a_{ij}$ has only five independent components, because its trace is equal to 1: $a_{kk} = {n_x}^2 + {n_y}^2 + {n_z}^2 = 1$. Thus, when all dislocation lines have the unit

vector $\mathbf{n} = (1, 0, 0)$, the anisotropic tensor $\mathbf{a}$ has the following form:

$$\mathbf{a} = \langle \mathbf{n} \otimes \mathbf{n} \rangle = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{5}$$

describing a network of dislocations completely polarized (see [8]-[10] for the analogy with the anisotropic tensor describing the anisotropy of quantized vortices in turbulent superfluid helium II).

## 3 Basic variables and fundamental laws

The object of our study is to describe some mechanical, thermal and thermoelectric behaviour of semiconductor crystals and superlattices with emphasis on the contribution of dislocations. It is assumed that the following fields interact with each other:

- the elastic field described by the stress tensor $\tau_{ij}$ and the small-strain tensor $\varepsilon_{ij}$,
- the thermal field described by the temperature $T$, its gradient and the heat flux $q_i$,
- the electromagnetic field described by the electromotive intensity $\mathcal{E}_i$ and the magnetic induction $B_i$,
- the charge carrier fields described by the concentrations of electrons $n$ and holes $p$ and their currents $j_i^n$ and $j_i^p$, respectively,
- the dislocation field described by the dislocation density tensor $a_{ij}$ and its gradient $a_{ij,k}$.

In contrast, it is assumed, for the sake of simplicity, that the interfaces between the alternating semiconductors (or, alternatively, the parallel grids in helium II, as mentioned in the introduction) are given and remain static, so that they are taken as parameters rather than as independent variables. In more general setting, it could be assumed that they are also variables, as the presence of many dislocations could induce some local curvature on them, but here we consider them as static filters for dislocations [2], [3]. Furthermore, here it is assumed that there is an external electric field $\tilde{\mathcal{E}}_i$, that is treated as an imposed parameter.

The independent constitutive variables, mentioned above, are represented by the set $C$ given by

$$C = \{\varepsilon_{ij}, \mathcal{E}_i, B_i, n, p, T, a_{ij}, j_i^n, j_i^p, q_i, n_{,i}, p_{,i}, T_{,i}, a_{ij,k}\}\,. \tag{6}$$

In particular, we will focus our attention on dislocations, described by $a_{ij}$, and $a_{ij,k}$, if nonlocal effects are relevant (as well as the quantized vortices in superfluids), but the macroscopic model is general enough to incorporate other kinds of defects.

The physical processes occurring in the above-defined situations are governed by two groups of laws (see [19]-[23]). The first group regards Maxwell equations and the classical balances of mass, momentum, and energy. The second group concerns the evolution of the internal variable $a_{ij}$, the currents of the electric charges $n$ and $p$, $j_i^n$, $j_i^p$ and the heat flux $q_i$. This specific choice allows to include the relaxation properties of the thermal field and charge carrier fields. However, we ignore the corresponding effect for the mechanical properties so that $\tau_{ij}$ is not in the set (6). Now, we consider, in Galilean approximation,

*Maxwell's equations* having the form

$$\varepsilon_{ijk}E_{k,j} + \frac{\partial B_i}{\partial t} = 0, \qquad D_{i,i} - \rho Z = 0, \tag{7}$$

$$\varepsilon_{ijk}H_{k,j} - j_i^Z - \frac{\partial D_i}{\partial t} = 0, \qquad B_{i,i} = 0, \tag{8}$$

where **E**, **B**, **D** and **H** denote the electric field, the magnetic induction, the electric displacement and the magnetic field per unit volume, respectively, and $\varepsilon_{ijk}$ is the Levi-Civita pseudo-tensor, completely antisymmetric. The variation of **E** and **B** would be of interest for the description of optical phenomena. Otherwise, **E** and **B** may be taken as parameters.

Moreover, it has been assumed that the magnetic and dielectric properties of the semiconductor are disregarded so that the magnetization and the polarization of the body are null, and then $H_i = \frac{1}{\mu_0}B_i, \qquad E_i = \frac{1}{\varepsilon_0}D_i,$ with $\varepsilon_0$ and $\mu_0$ the permittivity and permeability of vacuum, respectively. In [20] a model for a polarized semiconductor was formulated.

The concentration of the total charge $Z$ and the density of the total electric current $\mathbf{j}^Z$ are defined as follows

$$Z = n + p, \quad j_i^Z = \rho Z v_i + j_i^n + j_i^p, \tag{9}$$

$$\text{with} \quad j_i^n = \rho n(v_i^n - v_i), \quad j_i^p = \rho p(v_i^p - v_i), \tag{10}$$

where $\rho$ denotes the mass density, $n$ ($n < 0$) is the concentration of the negative electric charge density (coming from the density of the free electrons given by doping the semiconductor by pentavalent impurities and the density of the intrinsic semiconductor base free electrons), $p$ ($p > 0$) is the concentration of total positive electric charge (coming from the concentration of the holes produced by doping the semiconductor by trivalent impurities and the concentration of the intrinsic semiconductor base holes), $\mathbf{j}^Z$ is the density of the total electric current, $v_i$ is the barycentric velocity of the body, $v_i^n$, and $v_i^p$, are the velocities of concentrations of electric charges $n$ and $p$, and $j_i^n$, and $j_i^p$, their currents (i.e. the electric currents due to the relative motion of the electric charges respect to the barycentric motion of the body). The sum of these last currents gives the conduction electric current, $\rho Z v_i$ is the electric current due to convection.

Thus, we have the following charge conservation laws

$$\rho\dot{n} + j_{i,i}^n = g^n, \quad \rho\dot{p} + j_{i,i}^p = g^p, \tag{11}$$

where the superimposed dot denotes the material derivative and $g^n$ and $g^p$ represent sources of negative and positive charges, respectively, describing the recombination of electrons and holes and satisfying the equation

$$g^n + g^p = 0.$$

In this description we have not taken into consideration the fixed ionized charges coming from the impurities.

Also, we have:
*the continuity equation*

$$\dot{\rho} + \rho v_{i,i} = 0, \tag{12}$$

where the mass of charge carriers has been neglected compared to $\rho$;
*the momentum balance*:

$$\rho\dot{v}_i - \tau_{ji,j} - \rho Z(\mathcal{E}_i + \tilde{\mathcal{E}}_i) - \varepsilon_{ijk}\left(j_j^n + j_j^p\right) B_k - f_i = 0, \tag{13}$$

where $\mathcal{E}_i$ is the electric field referred to an element of the matter at time t, $\tilde{\mathcal{E}}_i$ is a given external electric field and $f_i$ is the body force;
*the internal energy balance*:

$$\rho\dot{U} - \tau_{ji}\frac{d\varepsilon_{ij}}{dt} - \left(j_j^n + j_j^p\right)(\mathcal{E}_j + \tilde{\mathcal{E}}_j) + q_{i,i} - \rho r = 0, \tag{14}$$

where $U$ is the internal energy density, $r$ is the heat source distribution and $\varepsilon_{ij}$ is the small strain tensor defined by

$$\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}) \quad (i, j = 1, 2, 3), \tag{15}$$

where $\mathbf{u}$ is the displacement field. Then, $\frac{d\varepsilon_{ij}}{dt}$ is given by

$$\frac{d\varepsilon_{ij}}{dt} = \frac{1}{2}\left(v_{i,j} + v_{j,i}\right) \quad (i,j = 1,2,3). \tag{16}$$

The rate equations for the dislocation tensor and the electron, hole and heat fluxes are introduced as ansatzes, in the form of balance equations, that, in a field formulation of thermodynamics, describe the time evolution of tensorial fields [34], [35]. Thus, assuming that dislocation lines can move through the crystal, the *evolution equation for the dislocations* reads

$$\dot{a}_{ij} + \mathcal{V}_{ijk,k} - A_{ij}(C) = 0, \tag{17}$$

where $\mathcal{V}_{ijk}$ and $A_{ij}$ are the dislocation flux tensor and the dislocation source, respectively. Here, we will take $\mathcal{V}_{ijk} = -Da_{ij,k}$, with $D$ a dislocation transport coefficient.

The last set of *evolution equations* concerns *electron*, *hole* and *heat fluxes*:

$$\dot{j}_i^n - J_i^n(C) = 0, \tag{18}$$

$$\dot{j}_i^p - J_i^p(C) = 0, \tag{19}$$

$$\dot{q}_i - Q_i(C) = 0, \tag{20}$$

where $J_i^n$, $J_i^p$ and $Q_i$ are the sources of carrier fluxes and heat flux, respectively. Usually, these fluxes are directly given by transport laws relating them to temperature and voltage gradients, but here we are considering them as independent variables. Taking $\mathbf{q}$ as independent variable allows to apply a slightly modified form of this model to the description of heat flow in turbulent helium II between a set of mutually parallel grids (in such case, of course, there would not be any flux of electric charge) [8]-[10]. In the equations (18)-(20) the fluxes of electron, hole and heat fluxes are not taken into consideration, because we have to obtain a balanced system of equations, where the number of equations is equal to the number of variables.

## 4 Entropy inequality and second-law restrictions

All the admissible solutions of the proposed evolution equations (7)-(20) should be restricted by the second law of thermodynamics, expressed through the following *entropy inequality*

$$\rho\dot{S} + \phi_{k,k} - \frac{\rho r}{T} \geq 0, \tag{21}$$

where S denotes the entropy per unit mass and $\phi_k$ is the entropy flux associated with the fields of the set $C$.

The set of constitutive functions (dependent variables) is thus given by:

$$W = \{\tau_{ij}, U, g^n, g^p, A_{ij}, J_i^n, J_i^p, Q_i, S, \phi_i, \mu^n, \mu^p, \pi_{ij}\}\,. \tag{22}$$

The electrochemical potentials $\mu^n$ and $\mu^p$ for electrons and holes and the similar potential $\pi_{ij}$ conjugated to $n, p$ and $a_{ij}$, respectively, will appear in the sequel.
Then, we must look for general constitutive equations in the form:

$$W = \tilde{W}(C), \tag{23}$$

where both $C$ and $W$ are evaluated at the same point and time.

Among the various methods to analyze the entropy inequality, in [19] one of the most efficient was chosen, that is based on Liu's theorem [33], where all balance and evolution equations of the problem are considered as mathematical constraints for its physical validity. This theorem is used in rational extended thermodynamics, that uses procedures different from that ones used in the extended irreversible thermodynamics, stemming from CIT (classical irreversible thermodynamics), that exploits the dissipation inequality as in CIT [14], [34]-[37].

Introducing the free energy density $F = F(C)$, by

$$F = U - TS, \tag{24}$$

assuming the mass density $\rho$ is practically constant, neglecting the body force and the heat source distribution, in [19] the following results (and others) were derived: the *laws of state*, giving the partial derivatives of the free energy in terms of the respective conjugated thermodynamic variables:

$$\begin{gathered}
\rho\frac{\partial F}{\partial \varepsilon_{ij}} = \tau_{ij}, \qquad \rho\frac{\partial F}{\partial \mathcal{E}_i} = 0, \qquad \rho\frac{\partial F}{\partial B_i} = 0, \\
\rho\frac{\partial F}{\partial a_{ij}} = \pi_{ij}, \qquad \frac{\partial F}{\partial n} = \mu^n, \qquad \frac{\partial F}{\partial p} = \mu^p, \qquad \frac{\partial F}{\partial T} = -S, \\
\frac{\partial F}{\partial n_{,i}} = 0, \qquad \frac{\partial F}{\partial p_{,i}} = 0, \qquad \frac{\partial F}{\partial T_{,i}} = 0, \qquad \frac{\partial F}{\partial a_{ij,k}} = 0,
\end{gathered} \tag{25}$$

furthermore, the *generalized affinities* conjugated to the respective fluxes of $n$, $p$ and $U$ were generalized:

$$\rho\frac{\partial F}{\partial j_i^n} = \Pi_i^n, \qquad \rho\frac{\partial F}{\partial j_i^p} = \Pi_i^p, \qquad \rho\frac{\partial F}{\partial q_i} = \Pi_i^q. \tag{26}$$

The corresponding *residual inequality*, expressing the positive character of entropy production, is

$$T\frac{\partial\phi_k}{\partial n}n_{,k}+T\frac{\partial\phi_k}{\partial p}p_{,k}+T\frac{\partial\phi_k}{\partial a_{ij}}a_{ij,k}+T\frac{\partial\phi_k}{\partial T}T_{,k}+$$

$$+(j_k^n+j_k^p)(\mathcal{E}_k+\tilde{\mathcal{E}}_k)-\pi_{ij}A_{ij}-\Pi_i^nJ_i^n-$$

$$-\Pi_i^pJ_i^p-\Pi_i^qQ_i-\mu^ng^n-\mu^pg^p\geq 0. \tag{27}$$

Note that (27) restricts the possible relations between the sources $J_i^n$, $J_i^p$ and $Q_i$ appearing in (18)-(20) and the generalized affinities $\Pi_i^n$, $\Pi_i^p$, $\Pi_i^q$ appearing in (26).

The entropy flux $\phi_k$ contains contributions of the fluxes of $U$, $n$, $p$ and $a_{ij}$ multiplied by the corresponding conjugated variables $\frac{1}{T}$ , $-\frac{\mu^n}{T}$ and $-\frac{\mu^p}{T}$, $-\frac{\pi_{ij}}{T}$

$$\phi_k=\frac{1}{T}(q_k-\mu^nj_k^n-\mu^pj_k^p-\pi_{ij}\mathcal{V}_{ijk}). \tag{28}$$

From (25) it follows that the free energy $F$ is a function depending on the set of independent variables

$$C_1=C_1(\varepsilon_{ij},\mathcal{E}_i,n,p,T,a_{ij},j_i^n,j_i^p,q_i), \tag{29}$$

$$F=F(C_1). \tag{30}$$

In [20], analyzing the entropy inequality by Liu's theorem in a model for a polarized semiconductor, where the flux of dislocation tensor was considered as independent variable, among the obtained results some of them are a generalization of the above results (25)- (30), derived in [19].

## 5 Constitutive theory

In this paper one of our objectives is deriving the constitutive equations, up to first order in the perturbations of the variables, consistent with the restrictions of the second law, derived in Section 4, through (25)-(27), and with a particular assumption for the free energy $F$ (see (30)). We expand the free energy $F=U-TS$, around a reference state of thermodynamic equilibrium, characterized by

$$(T)_0=T_0,\quad (\epsilon_{ij})_0=\epsilon_{ij0}=0,\quad (n)_0=n_0,\quad (p)_0=p_0,\quad (a_{ij})_0=a_{ij0},$$
$$(\tau_{ij})_0=\tau_{ij0}=0,\quad (\pi_{ij})_0=\pi_{ij0}=0,\quad (\mu^p)_0=\mu_0^p=0,\quad (\mu^n)_0=\mu_0^n=0, \tag{31}$$

$(S)_0 = S_0,\ (U)_0 = U_0,\ (\Pi_i^n)_0 = \Pi_{i0}^n = 0,\ (\Pi_i^p)_0 = \Pi_{i0}^p = 0,\ (\Pi_i^q)_0 = \Pi_{i0}^q = 0.$

Also, we denote by

$$\theta = T - T_0,\ |\frac{\theta}{T_0}| \ll 1,\ \mathcal{N} = n - n_0, |\frac{\mathcal{N}}{n_0}| \ll 1,$$

$$\mathcal{P} = p - p_0,\ |\frac{\mathcal{P}}{p_0}| \ll 1, \alpha_{ij} = a_{ij} - a_{ij0},\ |\frac{a_{ij}}{a_{ij0}}| \ll 1, \tag{32}$$

deviations with respect to equilibrium state (denoted by the subscript "$_0$"), and we neglect in the expansion of $F$ the terms of order higher than the second one.

## 5.1 Equation for the free energy

The expansion of the free energy (30) up to second-order approximation in the deviations of the independent variables, with respect to the considered thermodynamic equilibrium state, has in principle the form

$$F - F_0 = \frac{1}{2\rho} c_{ijlm}\varepsilon_{ij}\varepsilon_{lm} - \frac{\lambda_{ij}^{\theta\epsilon}}{\rho}\theta\varepsilon_{ij} + \frac{\lambda_{ijlm}^{a\epsilon}}{\rho}\varepsilon_{ij}\alpha_{lm} -$$

$$\frac{1}{2}\frac{c}{T_0}\theta^2 - \frac{\lambda_{ij}^{a\theta}}{\rho}\alpha_{ij}\theta + \frac{\lambda_{ijlm}^{a}}{2\rho}\alpha_{ij}\alpha_{lm} + \frac{\lambda^{\mathcal{N}}}{2}\mathcal{N}^2 + \frac{\lambda^{\mathcal{P}}}{2}\mathcal{P}^2 +$$

$$\frac{1}{2\rho}\lambda_{ij}^{qq} q_i q_j + \frac{1}{2\rho}\lambda_{ij}^{j^n j^n} j_i^n j_j^n + \frac{1}{2\rho}\lambda_{ij}^{j^p j^p} j_i^p j_j^p - S_0\theta, \tag{33}$$

where we have taken into account the state laws, the definitions of affinities (25) and (26), the assumptions (31) and (32), we have focused our attention on some effects of dislocations (related to $\alpha_{ij}$), of the small deformations $\varepsilon_{ij}$, of the temperature $\theta$, of the relaxation effects of the fluxes $j_i^n, j_i^p, q_i$ and of the presence of the charges $\mathcal{N}$ and $\mathcal{P}$, the terms not related to our purpose have been disregarded. Also, in (33) the property that $F$ is invariant under time reversal was used, so that the terms of first order containing the fluxes are null. Some of the coefficients appearing in (33) have well-known physical meanings: $c$ is the specific heat, $c_{ijlm}$ the elastic tensor, $\lambda_{ij}^{\theta\epsilon}$ the thermoelastic constants, $\lambda_{ijkl}^{a}$, $\lambda^{\mathcal{N}}$ $\lambda^{\mathcal{P}}$ are the diffusion constants for dislocations and charges and the coefficients $\lambda_{ij}^{qq}$, $\lambda_{ij}^{j^n j^n}$, $\lambda_{ij}^{j^p j^p}$ are proportional to the relaxation times of the fluxes $\mathbf{q}$, $\mathbf{j}^n$, $\mathbf{j}^p$. The other quantities $\lambda_{ij}^{\theta\epsilon}$, $\lambda_{ijlm}^{a\epsilon}$, $\lambda_{ijlm}^{a\theta}$ express the interactions among the various fields inside the system discussed below.

These phenomenological coefficients, that are supposed constant, satisfy the following symmetry relations

$$c_{ijlm} = c_{lmij} = c_{jilm} = c_{ijml} = c_{jiml} = c_{mlij} = c_{mlji} = c_{lmji}, \tag{34}$$

$$\lambda_{ij}^{\theta\epsilon} = \lambda_{ji}^{\theta\epsilon}, \quad \lambda_{ijlm}^{a\epsilon} = \lambda_{jilm}^{a\epsilon} = \lambda_{lmji}^{a\epsilon} = \lambda_{lmij}^{a\epsilon}, \tag{35}$$

$$\lambda_{ijlm}^{a} = \lambda_{lmij}^{a}, \quad \lambda_{ij}^{qq} = \lambda_{ji}^{qq}, \quad \lambda_{ij}^{j^n j^n} = \lambda_{ji}^{j^n j^n}, \quad \lambda_{ij}^{j^p j^p} = \lambda_{ji}^{j^p j^p}, \tag{36}$$

In (33) the phenomenological coefficients, with their symmetry properties, come from the physical interpretation of the second partial derivatives of free energy respect to the considered independent variables, with their properties of invariance respect to the priority of derivation with respect to the considered variables. Furthermore, the symmetry of the small strain tensor $\varepsilon_{ij}$ is taken into consideration and also the physical dimensions of the physical quantities multiplying the various terms of approximation in $F$. Also, the introduction of minus sign comes from physical reasons. The particular values of these coefficients will depend on the structure of the anisotropic semiconductor crystals and superlattices considered, which will imply that some of them are vanishing. For instance, in the superlattice of Fig.2, direction $x$ perpendicular to the interfaces is clearly different than directions $y$ and $z$. In general terms, one would describe the geometry of the superlattice by means of a tensor (taken as a parameter rather than as a variable), and use this tensor in the construction of some additional terms of the free energy $F$.

### 5.2 Equations of state

By virtue of (25), (26) we obtain for the equations of state for $S, \tau_{ij}, \pi_{ij}$, and the generalized affinities conjugated to the fluxes $\Pi_i^q, \Pi_i^n, \Pi_i^p$:

$$\tau_{ij} = c_{ijlm}\varepsilon_{lm} - \lambda_{ij}^{\theta\epsilon}\theta + \lambda_{ijlm}^{a\epsilon}\alpha_{lm}, \tag{37}$$

$$S = S_0 + \frac{\lambda_{ij}^{\theta\epsilon}}{\rho}\varepsilon_{ij} + \frac{c}{T_0}\theta + \frac{\lambda_{ij}^{a\theta}}{\rho}\alpha_{ij}, \tag{38}$$

$$\pi_{ij} = \lambda_{ijlm}^{a\epsilon}\varepsilon_{lm} - \lambda_{ij}^{a\theta}\theta + \lambda_{ijlm}^{a}\alpha_{lm}, \tag{39}$$

$$\mu^n = \lambda^{\mathcal{N}}\mathcal{N}, \tag{40}$$

$$\mu^p = \lambda^{\mathcal{P}}\mathcal{P}. \tag{41}$$

In (37)-(39) the physical meaning of $\lambda_{ij}^{a\theta}$ and of $\lambda_{ijlm}^{a\epsilon}$ is the influence of $\theta$ and of $\epsilon_{ij}$ on the dislocation field $\alpha_{ij}$. For instance if $\lambda_{ij}^{a\theta}$ is positive, increasing the

temperature $\theta$ the dislocations potential $\pi_{ij}$ will decrease. Thus, dislocations go from the zone of lower $\theta$ to that of higher $\theta$ (the opposite would be true if $\lambda_{ij}^{a\theta}$ is negative). This behaviour will be relevant when the temperature of the system is not homogeneous. An analogous information is contained in $\lambda_{ijlm}^{a\epsilon}$: if positive, dislocations will go from regions with higher $\epsilon_{ij}$ to those with lower $\epsilon_{ij}$ and viceversa. Below we will briefly return to this point.

Regarding the *affinities* (each one conjugated to own flux) we obtain

$$\Pi_i^q = \lambda_{ij}^{qq} q_j, \tag{42}$$

$$\Pi_i^n = \lambda_{ij}^{j^n j^n} j_j^n, \tag{43}$$

$$\Pi_i^p = \lambda_{ij}^{j^p j^p} j_j^p. \tag{44}$$

According to EIT (extended irreversible thermodynamics) [11]-[13] the coefficients $\lambda_{ij}^{qq}$, $\lambda_{ij}^{j^n j^n}$ and $\lambda_{ij}^{j^p j^p}$ are proportional to the relaxation times of $\mathbf{j}^n$, $\mathbf{j}^p$ and $\mathbf{q}$, in isotropic systems $\lambda_{ij}^{qq} = \tau^q \delta_{ij}$, $\lambda_{ij}^{j^n j^n} = \tau^{j^n} \delta_{ij}$ and $\lambda_{ij}^{j^p j^p} = \tau^{j^p} \delta_{ij}$. These equations are necessary because, as we have commented above, the residual inequality (27) sets a strong connection between the source terms in (18)-(20) and the generalized affinities given by (42)-(44).

### 5.3 Rate equations for the fluxes and the internal variable

Regarding the rate equations for the charges and heat fluxes and the dislocation tensor, choosing particular expressions for the sources terms $A_{ij}$, $Q_i$, $J_i^n$, $J_i^p$ (that are constitutive functions), we obtain for the dislocations

$$\tau^\alpha \dot{\alpha}_{ij} = D\alpha_{ij,kk} - \alpha_{ij}, \tag{45}$$

whereas for the fluxes one gets

$$\tau^{j^n} \dot{j}_i^n = \Sigma^n \tilde{\mathcal{E}}_i - \chi^n \theta_{,i} + \eta^1 q_i - j_i^n + \eta^2 j_i^p + \eta^3 \alpha_{jj,i}, \tag{46}$$

$$\tau^{j^p} \dot{j}_i^p = \Sigma^p \tilde{\mathcal{E}}_i - \chi^p \theta_{,i} + \omega^1 q_i + \omega^2 j_i^n - j_i^p + \omega^3 \alpha_{jj,i}. \tag{47}$$

$$\tau^q \dot{q}_i = -\Sigma^q \tilde{\mathcal{E}}_i - \chi^q \theta_{,i} - q_i + \lambda^1 j_i^n + \lambda^2 j_i^p + \lambda^3 a_{jj,i}, \tag{48}$$

where $\tau^\alpha$, $\tau^{j^n}$, $\tau^{j^p}$, $\tau^q$ are the relaxation times of the fields $\boldsymbol{\alpha}$, $\mathbf{j}^n$, $\mathbf{j}^p$ and $\mathbf{q}$, respectively, the phenomenological coefficients are constant and in particular $\Sigma^n$, $\Sigma^p$ are conductivities, $\Sigma^q$ is Peltier constant, $\chi^n$, $\chi^p$ are Seebeck coefficients, $\chi^q$ is the heat conductivity coefficient, the other phenomenological coefficients describe interactions between the different fields present

in the examined media. In this case the defective semiconductors (and superlattices) under consideration are isotropic, having symmetry properties invariant under orthogonal transformations with respect to all rotations and to inversion of the frame of Cartesian axes [15]. Furthermore, we have considered only the influence of the fields related to our purpose to illustrate a relevant technological application: *the thermoelectric case.*
The rate equation (48) for the heat flux generalizes Vernotte-Cattaneo relation, where the finite velocity of the thermal disturbances is taken into consideration. Also in (45), (46) and (47) the relaxation properties of the dislocation and charge fields are described. Usually, heat flux and electric flux are given by transport equations relating them to temperature gradient and to voltage gradient. Here, following the philosophy of the extended irreversible thermodynamics, we have considered them as independent variables with their own evolution equations.

## 5.4 Conditions at the interfaces

The set of equations (45)-(48) could be complemented with additional terms describing the role of the interfaces on heat transport, charge transport and dislocation transport. For instance, in an interface between A and B semiconductors, a heat flux $\mathbf{q}$ would imply a temperature jump $\theta_A - \theta_B = R_{AB}\mathbf{q}$, with $R_{AB}$ being the thermal boundary resistence of the interface. Analogously, dislocation filtering through an interface would lead to a discontinuity of $\pi_{ijA} - \pi_{ijB}$, being $\pi_{ij}$ the thermodynamic conjugate to $a_{ij}$ given in (25) and modelized in (39). Such jump of $\pi_{ij}$ at the interface would be proportional to the resistence of the interface to the flow of dislocation through it. In particular, for the dislocations across an interface we will have

$$\pi_{xxA} - \pi_{xxB} = R^x_{AB}\dot{\alpha}_{xx},$$

$$\pi_{yyA} - \pi_{yyB} = R^y_{AB}\dot{\alpha}_{yy},$$

where $R^x_{AB}$ and $R^y_{AB}$ are the resistences of the interface to the transfer of dislocations orthogonal to the interface (which is in the plane $yz$) or parallel to interface, respectively. In equilibrium the dislocation flux would be zero and the dislocations density would vary according to $\pi_{xx}$ =constant, $\pi_{yy}$ =constant, along the longitudinal real $x$ axis. Combining this with expression (39) for $\pi_{ij}$, in terms of $\theta$, $\alpha_{lm}$ and $\varepsilon_{lm}$, $\alpha_{lm}$ in the different parallel layers of the superlattice would be obtained in terms of $\theta$ and $\varepsilon_{lm}$.

# 6 Conclusions

In this paper we have dealt with the basic laws of non-equilibrium thermodynamics applied to the description of semiconductor crystals and superlattices with dislocations. We have only aimed to give a general view of the theoretical framework, without entering into specific details. In contrast with previous works, where dislocations are described by means of a scalar thermodynamic variable ($\rho_D$, the dislocation lenght density per unit volume), we have dealt here with a tensorial description of dislocations in terms of the dislocation tensor $\alpha_{ij}$. Furthermore, we have assumed that the heat flux and the fluxes of electric carriers are also independent variables with their evolution equations, according to extended thermodynamics. These hypoteses have made that the corresponding equations, in first-order in the deviations from equilibrium, become very cumbersome, but this complexity is unavoidable to describe the system. Thus, we have skipped all the intermediate details and we have given directly the resulting equations compatible with the thermodynamic formalism.

Particular applications of this formalism could be, for instance, the analysis of dislocation filtering through interfaces, which act as stopping barriers for the motion of dislocations. This has practical applications to avoid flow stress behaviour and plastic effects, or to control the dislocation density inside each layer. Also, a modification of this formalism (eliminating electric transport effects) could be applied to the description of grid-generated quantum turbulence in superfluid helium II, as it has been mentioned in the introduction. Thus, the general framework proposed here seems to be very promising for applications.

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