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A NON CONVENTIONAL THERMODYNAMICAL MODEL FOR NANOCRYSTALS WITH DEFECTS OF DISLOCATION *

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Abstract

In the framework of the extended irreversible thermodynamics a non conventional description for nanocrystals with defects of dislocation is given, introducing a second order dislocation tensor *à* la Maruszewski, its gradient and its flux as internal variables in the thermodynamic state vector. Liu's theorem is used to analyze the entropy inequality and to derive the laws of state, the affinities, the entropy flux and the residual inequality. To close the system of equations illustrating the behaviour of the media under consideration, the constitutive equations and the rate equations for the dislocation field, its flux and the heat flux, presenting a relaxation time and describing disturbances propagating with finite velocity, are derived, in a first approximation. The behaviour of dislocation defects in nanostructures is one of the challenges in the so called "defects engineering", because they have a direct influence on mechanical and transport properties. The obtained results have applications in nanotechnology and several fields of applied sciences.

1 Introduction

The models for nanocrystals with defects of dislocation may have relevance in many fundamentals sectors of nanotechnology. Understanding the influence of dislocations on mechanical and transport properties in miniaturized

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systems is an interesting topic in "dislocation engineering". Here, in the framework of the extended irreversible thermodynamics (see [1], [2], [3], [4], [5], [6], [7], [8], [9], [10]), nanocrystals with dislocation lines are described, using an internal variable, the dislocation core tensor, its gradient and its flux. Dislocation channels modify the thermal conductivity. In [11] and [12] non-equilibrium temperatures and heat transport equation in nanocrystals with defects of dislocation were studied using the results obtained in this paper. From experimental and theoretical studies it was found that the dislocation density ρ_d, described by the trace of the dislocation core tensor, has only a minor effect on the thermal conductivity for defects densities smaller than a characteristic value dependent on the material and temperature but for higher values, there is a decrease of thermal conductivity. This is due to phonon-defect scattering, which is negligible as compared to phonon-phonon scattering for small defects densities ρ_d but leads to a reduction in the thermal conductivity or high values of ρ_d, and this situation influences the nanodevice performances. Nanostructures can present metallurgical defects (for example inclusions, cavities, microfissures, dislocations), that sometimes can self propagate because of changed conditions and surrounding conditions that are favorable. A relatively high temperature gradient could produce, for instance, a migration of defects inside the system. In [13], [14], [15], [16], [17], [18], [19], [20], [21], [22] [23], [24], [25], [26], porous, piezoelectric, elastic, semiconductor and superlattice stuctures with dislocation defects were also studied using the same internal variable (the dislocation core tensor), its gradient and its flux. The results, obtained in this paper, may have applications in describing the thermal behavior in nanosystems, where the phenomena are fast and the rate of variation of the properties of the system is faster than the time scale characterizing the relaxation of fluxes towards their respective local-equilibrium value. In these nanosystems, situations of high-frequency thermal waves occur. In this case, the thermal perturbation is so fast that its frequency becomes of the order of the reciprocal of the internal relaxation time, given, for instance, by the collision time of heat carriers. Furthermore, the volume element size d of these systems along some direction is so small that it becomes comparable to (or smaller than) the mean-free path l of the heat carriers ($d \leq l$). Then, in extended thermodynamics it is essential to incorporates the fluxes among the state variables. In Section 2, in the framework of extended irreversible thermodynamics with internal variables, a model is developed for elastic nanosystems with dislocations, where the internal structure is described by a dislocation core tensor *à* la Maruszewski (see [27]), its gradient and its flux. In [24], [25] a new definition of dislocation tensor was used, introduced in analogy with the anisotropic tensor describing the anisotropy of quantized vortices in turbulent superfluid helium II [28], [29] and [30]. In Section 3 the entropy inequality is analized, using Liu's theorem [31] and several results are obtained: the laws of state, the affinities, the flux-like properties of the physical processes inside the medium, the residual inequality, the entropy flux and the form of the free energy. These results are taken into consideration in [11] and [12], where, however, the flux of dislocations was negligible in the thermodynamic state vector and non-equilibrium temperatures and the heat transport for nanosystems with dislocations were studied. Instead, in this paper we take also into account that the dislocations can self propagate because of changed conditions, and this propagation may influence the heat proagation. In Section 4, by the help of Smith's theorem [32], that uses isotropic polynomial representations of proper functions obeying the principle of objectivity, the constitutive theory and the rate equations for the dislocation core tensor, the heat and dislocation fluxes are obtained, in a first approximation. According the extended thermodynamics a generalized Maxwell-Cattaneo-Vernotte and transport equations for the internal variable and the dislocation flux describing physical disturbances with finite velocity are derived, from which it is seen the influence of dislocation field on the processes occurring inside the media under consideration. The derived results have technological applications in very miniaturized systems (nanotechnology), in high-frequency processes and in the production of new materials having complex microstructures and special thermal properties.

2 A model for nanocrystals with dislocations

In this section in the framework of extended irreversible thermodynamics with internal variables, we present a model for nanocrystals with dislocations. The dislocation lines form a network of infinitesimally capillary channels, that disturb the periodicity of the crystal lattice, influence physical phenomena and interact with physical fields occurring inside the nanocrystals. The interatomic distances are not conserved in the direct neighborhood of a dislocation line. The diameter of the core is comparable with the lattice parameter and depends on the kind of dislocation [33], [34]. In this paper, among the various descriptions of media defective by dislocations we use that one based on using a dislocation core tensor a_{ij}, introduced by Maruszewski [27], coming from the use of volume and area averaging procedures. An elementary sphere volume Ω is considered, $\Omega = \Omega^s + \Omega^{ch}$, with Ω^s the solid space and Ω^{ch} the space with the dislocation channels. Furthermore, the

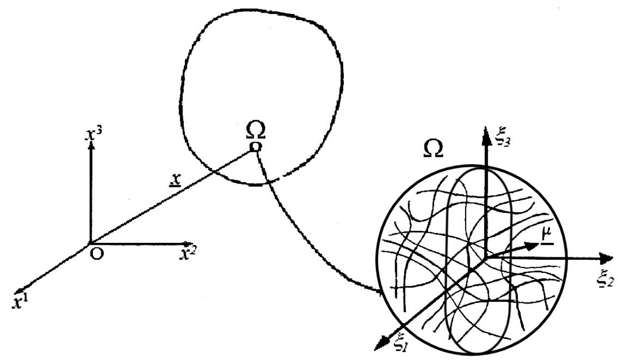

Figure 1: The averaging scheme [12]

central sphere section is indicated by Γ and is given by $\Gamma = \Gamma^s + \Gamma^{ch}$, with Γ^s and Γ^{ch} the solid area and the channel area of Γ. The orientation of Γ in Ω is given by the normal vector $\boldsymbol{\mu}$. All the microscopic quantities are described with respect to a system of coordinates ξ_i $(i = 1, 2, 3)$. while the macroscopic quantities are described with respect to a system of coordinates x_i $(i = 1, 2, 3)$. In Fig.1 we see the averaging scheme regarding an elementary volume with dislocation lines. The coefficient $f_v = \frac{\Omega^{ch}}{\Omega}$ is assumed constant inside the medium. Then, let $\boldsymbol{\eta}(\boldsymbol{\xi})$ be any scalar, spatial vector or any order tensor, describing at microscopic level the flux of some physical field, flowing through the channel space Ω^{ch}, with respect to the $\boldsymbol{\xi}$ coordinates. We assume that such quantity is zero in the solid space Ω^s and on the Γ^s. In such a medium Maruszewski [27] defines the so called dislocation tensor, responsible for the anisotropic structure of the dislocations lines, in the following way:

$$\bar{\eta}_i(\mathbf{x}) = r_{ij}(\mathbf{x}) \overset{*}{\eta}_j (\mathbf{x}). \tag{1}$$

Eq. (1) gives a linear mapping between the bulk-volume average quantity $\bar{\boldsymbol{\eta}}(\mathbf{x})$ and the channel area average $\overset{*}{\boldsymbol{\eta}} (\mathbf{x})$ of the same quantity passing through the dislocation area Γ^{ch} of central sphere section, respectively, given by

$$\bar{\boldsymbol{\eta}}(\mathbf{x}) = \frac{1}{\Omega} \int_{\tilde{\Omega}} \boldsymbol{\eta}(\xi) d\tilde{\Omega}, \quad \boldsymbol{\xi} \in \Omega^{ch}, \quad \overset{*}{\boldsymbol{\eta}}(\mathbf{x}) = \frac{1}{\Gamma^{ch}} \int_{\tilde{\Gamma}} \boldsymbol{\eta}(\boldsymbol{\xi}) d\tilde{\Gamma}, \quad \boldsymbol{\xi} \in \Gamma^{ch}, \tag{2}$$

where $\boldsymbol{\eta}(\mathbf{x})$ describes the flux of the physical field under consideration at macroscopic level. In [27] Maruszewski introduces a new tensor a_{ij}, that refers r_{ij} to the central sphere section Γ and is defined in the following way

$$a_{ij}(\mathbf{x}) = \Gamma^{-1} r_{ij}(\mathbf{x}). \tag{3}$$

a_{ij} is called *dislocation core tensor* and has unit m^{-2}.

2.1 Main equations

The aim of this paper is to derive the laws of state and a complete set of relations contributing to modeling a crystal defective by a network of dislocations. The mechanical properties of the considered system are described by the total stress tensor σ_{ij} (in general non symmetric) related to the whole body and the small-strain tensor ε_{ij} describing the deformation of the nanocrystal, $\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$, (where u_i are the components of the displacement vector field) so that the gradient of the velocity field v_i of the body is given by

$$v_{i,j} = w_{ij} + \frac{d\varepsilon_{ij}}{dt}, \tag{4}$$

where

$$\frac{d\varepsilon_{ij}}{dt} = \frac{1}{2}(v_{i,j} + v_{j,i}), \quad w_{ij} = \frac{1}{2}(v_{i,j} - v_{j,i}) \tag{5}$$

are the symmetric and the antisymmetric part of $v_{i,j}$, respectively. Since during the deformation the network of dislocations evolves in time, we assume that the dislocation field is described by the tensor a_{ij} (not necessarily symmetric), its gradient and its flux $\mathcal{V}_{ijk}$. Finally, the thermal field is governed by the temperature, its gradient and the heat flux q_i. Thus, the thermodynamic vector space is chosen as follows

$$C = \{\varepsilon_{ij}, T, a_{ij}, q_i, \mathcal{V}_{ijk}, T_{,i}, a_{ij,k}\}, \tag{6}$$

where we have taken into consideration the gradients $T_{,i}$ and $a_{ij,k}$. The choice of the independent variables shows that the relaxation properties of the thermal field and the dislocation field are taken into account in agreement with the general philosophy of the extended thermodynamics, however we ignore the relaxation properties and viscous effects of the mechanical field. All the processes occurring in the considered body are governed by two groups of laws. The first group concerns the classical balance equations: *the continuity equation*

$$\dot{\rho} + \rho v_{i,i} = 0, \tag{7}$$

where ρ denotes the mass density, v_i is the velocity of the body point and a superimposed dot denotes the material derivative;

the *momentum balance*

$$\rho \dot{v}_i - \sigma_{ji,j} - f_i = 0, \tag{8}$$

where f_i denotes a body force;
the *moment of momentum balance*

$$\varepsilon_{ijk}\sigma_{jk} + c_i = 0, \tag{9}$$

where c_i is a couple per unit volume;
the *internal energy balance*

$$\rho \dot{e} - \sigma_{ji} v_{i,j} + q_{i,i} - \rho h = 0, \tag{10}$$

where e is the internal energy density and h is a heat source.

The second group of laws concerns the evolution equations of dislocation field, its flux and the heat flux. These rate equations are constructed obeying the objectivity and frame-indifference principles (see [35], [36] and [37]). They are chosen having the form

$$\overset{*}{a}_{ij} + \mathcal{V}_{ijk,k} - A_{ij}(C) = 0, \tag{11}$$

$$\overset{*}{q}_i - Q_i(C) = 0, \tag{12}$$

$$\overset{*}{\mathcal{V}}_{ijk} - V_{ijk}(C) = 0, \tag{13}$$

where A_{ij} is the source-like term for the dislocations, Q_i is the heat source and V_{ijk} is the source term for the dislocation flux. A_{ij}, Q_i, V_{ijk} are constitutive functions of the independent variables of the set C (see Eq. (6)). In Eqs. (12)-(13) the fluxes of the heat flux and the dislocation flux 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. In (11)-(13) the superimposed asterisk indicates the Zaremba-Jaumann derivative defined for a vector, a second rank tensor and a general rank tensor $\boldsymbol{\nu}$ as follows

$$\overset{*}{\nu}_i = \dot{\nu}_i - w_{ik}\nu_k, \quad \overset{*}{\nu}_{ij} = \dot{\nu}_{ij} - w_{ik}\nu_{kj} - w_{jk}\nu_{ik},$$

$$\overset{*}{\nu}_{k\ldots m} = \dot{\nu}_{k\ldots m} - w_{kq}\nu_{q\ldots m} - \ldots - w_{mq}\nu_{k\ldots q}. \tag{14}$$

In the following we use for w_{ij} (see (4) and (5)) the expression $w_{ij} = v_{i,j} - \frac{\partial \varepsilon_{ij}}{\partial t}$ for problems of approximation.

3 Analysis of the entropy inequality

To be sure that the physical processes occurring in the body under consideration are real, all considered processes should be admissible from the thermodynamical point of view and thus they should not contradict the second law. Thus, all the admissible solutions of the proposed evolution equations have to satisfy the following *entropy inequality*

$$\rho \dot{S} + \phi_{i,i} - \frac{\rho r}{T} \geq 0, \tag{15}$$

where S is the entropy per unit mass and ϕ_i is the entropy flux associated with the fields of the set C, given by (6). Thus, the following set of constitutive functions, dependent variables, has to be derived

$$W = \{\sigma_{ij}, \Pi^a_{ij}, c_i, e, A_{ij}, Q_i, V_{ijk}, S, \phi_i\}, \quad \text{with} \quad W = \tilde{W}(C), \tag{16}$$

where Π^a_{ij} is the potential related to the dislocation field and both C and W are evaluated at the same point and time. Among the various methods to analyze the entropy inequality (15) the most convenient one is based on Liu's theorem [31], where all balance and evolution equations are considered as mathematical constraints for the general validity of the inequality (15). Then, the system of equations (8), (10), (11), (12), (13) and the entropy inequality (15) can be presented, respectively, in the form

$$A_{\Delta\gamma} x_\gamma + B_\Delta = 0, \tag{17}$$

$$\alpha_\gamma x_\gamma + \beta \geq 0, \tag{18}$$

with $A_{\Delta\gamma}$, x_γ, B_Δ, α_γ, β defined in a suitable way (see (25)-(28) and the Appendix).

Thus, analyzing the entropy inequality by Liu's theorem, we have

$$\alpha_\gamma x_\gamma + \beta - \Lambda_\Delta (A_{\Delta\gamma} x_\gamma + \beta_\Delta) \geq 0, \quad \forall \quad x_\gamma, \tag{19}$$

$$(\alpha_\gamma - A_{\gamma\Delta}\Lambda_\Delta) x_\gamma + (\beta - \Lambda_\Delta B_\Delta) \geq 0, \quad \forall \quad x_\gamma \tag{20}$$

and then

$$\alpha_\gamma - A_{\gamma\Delta}\Lambda_\Delta = 0, \qquad \beta - \Lambda_\Delta B_\Delta \geq 0, \quad \forall \quad x_\gamma, \tag{21}$$

where the so called Lagrange-Liu multipliers Λ_Δ, accounting for Eqs. (8), (10), (11), (12) and (13) are defined by

$$\Lambda_\Delta = \left\{ \Lambda^v_i, \Lambda^e, \Lambda^a_{ij}, \Lambda^q_i, \Lambda^{\mathcal{V}}_{ijk}, \right\}. \tag{22}$$

The mass conservation law is not taken into consideration, because the density of considered defective crystals is supposed constant. Therefore, if the left-hand side of the laws (8), (10), (11), (12) and (13) are denoted, respectively, by $\mathcal{F}_i^v$, $\mathcal{F}^e$, $\mathcal{F}_{ij}^a$, $\mathcal{F}_i^q$ and $\mathcal{F}_{ijk}^{\mathcal{V}}$, the first requirement of Liu's theorem, gives (19) written in the form

$$\rho\frac{\partial S}{\partial t}+\rho v_k S_{,k}+\phi_{k,k}-(\Lambda_i^v\mathcal{F}_i^v+\Lambda^e\mathcal{F}^e+\Lambda_{ij}^a\mathcal{F}_{ij}^a$$

$$+\Lambda_i^q\mathcal{F}_i^q+\Lambda_{ijk}^{\mathcal{V}}\mathcal{F}_{ijk}^{\mathcal{V}}\geq 0. \tag{23}$$

i.e.

$$\rho\frac{\partial S}{\partial t}+\rho v_k S_{,k}+(\phi_k)_{,k}-\Lambda_i^v\left(\rho\frac{\partial v_i}{\partial t}+\rho v_j v_{i,j}-\sigma_{ji,j}\right)$$

$$-\Lambda^e\left(\rho\frac{\partial e}{\partial t}+\rho v_k e_{,k}-\sigma_{ji}v_{i,j}+q_{i,i}\right)$$

$$-\Lambda_{ij}^a\left(\frac{\partial a_{ij}}{\partial t}+v_k a_{ij,k}+\frac{\partial\varepsilon_{ik}}{\partial t}a_{kj}-v_{i,k}a_{kj}+\frac{\partial\varepsilon_{jk}}{\partial t}a_{ik}-v_{j,k}a_{ik}+\mathcal{V}_{ijk,k}-A_{ij}\right)$$

$$-\Lambda_i^q\left(\frac{\partial q_i}{\partial t}+v_j q_{i,j}+\frac{\partial\varepsilon_{ij}}{\partial t}q_j-v_{i,j}q_j-Q_i\right)$$

$$-\Lambda_{ijk}^{\mathcal{V}}\left(\frac{\partial\mathcal{V}_{ijk}}{\partial t}+v_r\mathcal{V}_{ijk,r}+\frac{\partial\varepsilon_{ir}}{\partial t}\mathcal{V}_{rjk}-v_{i,r}\mathcal{V}_{rjk}+\right.$$

$$\left.\frac{\partial\varepsilon_{jr}}{\partial t}\mathcal{V}_{irk}-v_{j,r}\mathcal{V}_{irk}+\frac{\partial\varepsilon_{kr}}{\partial t}\mathcal{V}_{ijr}-v_{k,r}\mathcal{V}_{ijr}-V_{ijk}\right)\geq 0, \tag{24}$$

where the mass force and the heat source have been neglected. The entropy inequality is an objective law, then in (23) Λ^e is an objective scalar function, Λ_i^v,Λ_i^q are objective polar vectorial functions, Λ_{ij}^a is an objective tensorial function of second order and $\Lambda_{ijk}^{\mathcal{V}}$ is an objective tensorial function of third order. Taking into account that the entropy function S, the stress tensor σ_{ij}, the entropy flux ϕ_i, the internal energy e are constitutive functions of the independent variables $\varepsilon_{ij}, T, a_{ij}, q_i, \mathcal{V}_{ijk}, T_{,i}, a_{ij,k}$, from (19) and (24) we obtain the following quantities

$$\alpha_\gamma=\left\{0;\rho\frac{\partial S}{\partial\varepsilon_{ij}};\rho\frac{\partial S}{\partial T};\rho\frac{\partial S}{\partial a_{ij}};\rho\frac{\partial S}{\partial q_i};\rho\frac{\partial S}{\partial\mathcal{V}_{ijp}};\rho\frac{\partial S}{\partial T_{,i}};\right.$$

$$\rho\frac{\partial S}{\partial a_{ij,p}};0;\rho v_k\frac{\partial S}{\partial\varepsilon_{ij}}+\frac{\partial\phi_k}{\partial\varepsilon_{ij}};\rho v_k\frac{\partial S}{\partial q_i}+\frac{\partial\phi_k}{\partial q_i};\rho v_k\frac{\partial S}{\partial\mathcal{V}_{ijp}}\delta_{kl}+\frac{\partial\phi_k}{\partial\mathcal{V}_{ijp}}\delta_{kl};$$

$$\rho v_k \frac{\partial S}{\partial T_{,i}} + \frac{\partial \phi_k}{\partial T_{,i}}; \rho v_k \frac{\partial S}{\partial a_{ij,p}} \delta_{lk} + \frac{\partial \phi_k}{\partial a_{ij,p}} \delta_{lk} \Bigg\}, \tag{25}$$

$$\{x_\gamma\} = \left\{ \frac{\partial v_i}{\partial t}; \frac{\partial \varepsilon_{ij}}{\partial t}; \frac{\partial T}{\partial t}; \frac{\partial a_{ij}}{\partial t}; \frac{\partial q_i}{\partial t}; \frac{\partial \mathcal{V}_{ijp}}{\partial t}; \frac{\partial T_{,i}}{\partial t}; \right.$$

$$\left. \frac{\partial a_{ij,p}}{\partial t}; v_{i,k}; \varepsilon_{ij,k}; q_{i,k}; \mathcal{V}_{ijp,l}; T_{,ik}; a_{ij,pl} \right\}, \tag{26}$$

$$\beta = \left\{ (\rho v_k \frac{\partial S}{\partial T} + \frac{\partial \phi_k}{\partial T}) T_{,k} + (\rho v_k \frac{\partial S}{\partial a_{ij}} + \frac{\partial \phi_k}{\partial a_{ij}}) a_{ij,k} \right\}, \tag{27}$$

$$B_\triangle = \{ -\frac{\partial \sigma_{kr}}{\partial T} T_{,k} - \frac{\partial \sigma_{kr}}{\partial a_{ij}} a_{ij,k}; \rho v_k \frac{\partial e}{\partial T} T_{,k} + \rho v_k \frac{\partial e}{\partial a_{ij}} a_{ij,k}; -A_{ij} + v_k a_{ij,k}; -Q_i; -V_{ijk} \} \tag{28}$$

and a matrix $\{A_{\Delta\gamma}\} = \{A^{m|n}\}$, whose the elements are collected in Appendix A. Furthermore, we have

$$\alpha_\gamma = \alpha_\gamma(y_\lambda), \quad \beta = \beta(y_\lambda), \; B_\Delta = B_\Delta(y_\lambda), \; x_\gamma = x_\gamma(y_\lambda), \; A_{\Delta\gamma} = A_{\Delta\gamma}(y_\lambda),$$

with

$$\{y_\lambda\} = \{v_i, \varepsilon_{ij}, T, a_{ij}, q_i, \mathcal{V}_{ijk}, T_{,i}, a_{ij,k}\}. \tag{29}$$

Thus, after some calculations, from (21) the following results are deduced

$$\Lambda_r^v \rho \delta_{ir} = 0,$$

from which we have

$$\Lambda_r^v = 0,$$

and also

$$
\begin{aligned}
&\rho\frac{\partial S}{\partial \varepsilon_{ij}} - \Lambda^e \rho \frac{\partial e}{\partial \varepsilon_{ij}} = -\sigma_{ji}\Lambda^e,\\
&\rho\frac{\partial S}{\partial T} - \Lambda^e \rho \frac{\partial e}{\partial T} = 0,\\
&\rho\frac{\partial S}{\partial a_{ij}} - \Lambda^e \rho \frac{\partial e}{\partial a_{ij}} = \rho\Lambda^a_{ij},\\
&\rho\frac{\partial S}{\partial q_i} - \Lambda^e \rho \frac{\partial e}{\partial q_i} = \Lambda^q_i,\\
&\rho\frac{\partial S}{\partial \mathcal{V}_{ijk}} - \Lambda^e \rho \frac{\partial e}{\partial \mathcal{V}_{ijk}} = \Lambda^{\mathcal{V}}_{ijk},\\
&\rho\frac{\partial S}{\partial T_{,i}} - \Lambda^e \rho \frac{\partial e}{\partial T_{,i}} = 0,\\
&\rho\frac{\partial S}{\partial a_{ij,k}} - \Lambda^e \rho \frac{\partial e}{\partial a_{ij,k}} = 0,\\
&\rho v_k\frac{\partial S}{\partial \varepsilon_{ij}} + \frac{\partial \phi_k}{\partial \varepsilon_{ij}} - \Lambda^e \rho v_k \frac{\partial e}{\partial \varepsilon_{ij}} = 0,\\
&\rho v_k\frac{\partial S}{\partial T_{,i}} + \frac{\partial \phi_k}{\partial T_{,i}} - \Lambda^e \rho v_k \frac{\partial e}{\partial T_{,i}} = 0,\\
&\rho v_k\frac{\partial S}{\partial \mathcal{V}_{ijp}} + \frac{\partial \phi_k}{\partial \mathcal{V}_{ijp}} - \Lambda^e \rho v_k \frac{\partial e}{\partial \mathcal{V}_{ijp}} = \Lambda^a_{ij}\delta_{pk} + v_k\Lambda^{\mathcal{V}}_{ijp},
\end{aligned}
\tag{30}
$$

$$
\begin{aligned}
&\rho v_k\frac{\partial S}{\partial q_i} + \frac{\partial \phi_k}{\partial q_i} - \Lambda^e \rho v_k \frac{\partial e}{\partial q_i} = \Lambda^e\delta_{ik} + v_k\Lambda^q_i,\\
&\rho v_k\frac{\partial S}{\partial a_{ij,k}} + \frac{\partial \phi_k}{\partial a_{ij,k}} - \Lambda^e \rho v_k \frac{\partial e}{\partial a_{ij,k}} = 0.
\end{aligned}
\tag{31}
$$

The residual inequality has the form

$$
\left[\rho v_k\frac{\partial S}{\partial T} + \frac{\partial \phi_k}{\partial T} - \Lambda^e \rho v_k \frac{\partial e}{\partial T}\right] T_{,k} + \left[\rho v_k\frac{\partial S}{\partial a_{ij}} + \frac{\partial \phi_k}{\partial a_{ij}} - \Lambda^e \rho v_k \frac{\partial e}{\partial a_{ij}}\right] a_{ij,k}
$$
$$
+\Lambda^a_{ik}A_{ik} + \Lambda^q_i Q_i + \Lambda^{\mathcal{V}}_{ijk}V_{ijk} \geq 0. \tag{32}
$$

Introducing the free energy density F and the flux vector K_i by

$$
F = e - TS, \quad \text{and} \quad K_i = \rho F v_i - T\phi_i, \tag{33}
$$

substituting these expressions into (30) and (31) we obtain
the *multiplier* Λ^e (see $30)_2$

$$
\Lambda^e = \frac{1}{T(\Theta)}, \tag{34}
$$

where Θ denotes the empirical temperature,
the remaining *multipliers*

$$\Lambda^a_{ij} = -\frac{1}{T}\Pi^a_{ij}, \tag{35}$$

$$\Lambda^q_i = -\frac{1}{T}\Pi^q_i, \quad \Lambda^{\mathcal{V}}_{ijk} = -\frac{1}{T}\Pi^{\mathcal{V}}_{ijk}, \tag{36}$$

the laws of state (giving the variables in terms of the partial derivatives of the free energy respect to own conjugate variables)

$$\sigma_{ij} = \rho\frac{\partial F}{\partial \varepsilon_{ij}},$$

$$S = -\frac{\partial F}{\partial T}, \qquad \Pi^a_{ij} = \frac{\partial F}{\partial a_{ij}}, \qquad \frac{\partial F}{\partial T_{,i}} = 0, \qquad \frac{\partial F}{\partial a_{ij,k}} = 0 \tag{37}$$

the affinities (the variables conjugated to the corresponding fluxes)

$$\Pi^q_i \equiv \rho\frac{\partial F}{\partial q_i}, \qquad \Pi^{\mathcal{V}}_{ijk} \equiv \rho\frac{\partial F}{\partial \mathcal{V}_{ijk}}. \tag{38}$$

Eq.s (34)-(38) give the physical meaning of Lagrange multipliers. Also, we obtain the group of relations pertaining to the *flux-like properties* of the physical processes occurring in the considered media

$$\frac{\partial K_k}{\partial \varepsilon_{ij}} = 0, \qquad \frac{\partial K_k}{\partial q_i} = -\delta_{ik} + v_k\Pi^q_i, \tag{39}$$

$$\frac{\partial K_k}{\partial \mathcal{V}_{ijp}} = \Pi^a_{ij}\delta_{pk} + v_p\Pi^{\mathcal{V}}_{ijk}, \quad \frac{\partial K_k}{\partial T_{,i}} = 0, \quad \frac{\partial K_k}{\partial a_{ij,p}} = 0. \tag{40}$$

From these results the *residual inequality* simplifies to

$$T\frac{\partial \phi_k}{\partial T}T_{,k} + T\frac{\partial \phi_k}{\partial a_{ij}}a_{ij,k} - \Pi^a_{ij}A_{ij} - \Pi^q_i Q_i - \Pi^{\mathcal{V}}_{ijk}\mathcal{V}_{ijk} \geq 0. \tag{41}$$

From (39) and (40), taking into account (33), (37) and (38), we obtain

$$K_k = -q_k + \Pi^a_{ij}\mathcal{V}_{ijk} + \rho v_k F. \tag{42}$$

Hence, the form of the entropy flux is given by

$$\phi_k = \frac{1}{T}(q_k - \Pi^a_{ij}\mathcal{V}_{ijk}). \tag{43}$$

From (43) it is seen that in the entropy flux there are the contributions due to the heat and dislocation tensor fluxes. Also, from the above considerations it results that the free energy is given by the following function

$$F = F(\varepsilon_{ij}, T, a_{ij}, q_i, \mathcal{V}_{ijk}), \tag{44}$$

and, the stress tensor σ_{ij} is symmetric, being ϵ_{ij} symmetric (see the state law $(37)_1$), and therefore in the momentum of momentum balance (9) the couple c_i vanishes.

4 Constitutive relations and rate equations

In this section, in order to have a closed system of equations having the same number of equations and unknown variables (independent and dependent), by the help of Smith's theorem [32], that uses isotropic polynomial representations of proper functions which must obey the principle of objectivity, the constitutive theory and the rate equations for the dislocation field, the heat and dislocation fluxes are derived, in a first approximation. The distribution of the dislocations forms a network of very thin tubes influencing mechanical and transport processes within the medium. In general, the arrangement of the dislocation lines is an anisotropic one. However, there exist situations where it is possible to assume that the quantities responsible for the dislocation field and its flux can be presented in the form

$$a_{ij} = a\delta_{ij}, \qquad A_{ij} = A\delta_{ij}, \qquad \Pi^a_{ij} = \Pi^a \delta_{ij},$$

$$\mathcal{V}_{ijk} = \mathcal{V}_k \delta_{ij}, \qquad V_{ijk} = V_k \delta_{ij}, \qquad \Pi^{\mathcal{V}}_{ijk} = \Pi^{\mathcal{V}}_k \delta_{ij}. \tag{45}$$

Taking into account that σ_{ij} is a symmetric tensor, $\Pi^q_i, \Pi^{\mathcal{V}}_i, V_i, Q_i$ are absolute vectors and S, Π^a, A are scalars, applying Smith's theorem [32] the following representations are obtained, in a first approximation, for the constitutive functions σ_{ij}, S, Π^a

$$\sigma_{ij} = \beta^1_\sigma \delta_{ij} + \beta^2_\sigma \varepsilon_{ij}, \tag{46}$$

$$S = \beta^1_s T + \beta^2_s a + \beta^3_s \varepsilon_{kk}, \tag{47}$$

$$\Pi^a = \beta^1_\pi T + \beta^2_\pi a + \beta^3_\pi \varepsilon_{kk}, \tag{48}$$

where the coefficients β^α_σ $(\alpha = 1, 2)$, $\beta^\gamma_s, \beta^\gamma_\pi$ $(\gamma = 1, 2, 3)$ can be functions of the following invariants

$$T, a, \varepsilon_{kk}, \varepsilon_{ij}\varepsilon_{ij}, \tag{49}$$

for *the affinities* Π^q and $Pi_i^{\mathcal{V}}$

$$\Pi_i^q = \beta_q^1 \mathcal{V}_i + \beta_q^2 q_i, \quad \Pi_i^{\mathcal{V}} = \beta_{\mathcal{V}}^1 \mathcal{V}_i + \beta_{\mathcal{V}}^2 q_i, \tag{50}$$

where $\beta_q^\delta, \beta_{\mathcal{V}}^\delta (\delta = 1, 2)$ can be depend on the invariants:

$$\mathcal{V}_i \mathcal{V}_i, q_i q_i, \mathcal{V}_i q_i. \tag{51}$$

Furthermore, in a first approximation, we can assume that the rate equations (11)-(13) have the following form, where we have expressed the dislocation source A, the heat source Q_i and the dislocation flux source V_k by the help of Smith's theorem

$$\overset{*}{a} + \mathcal{V}_{k,k} = \gamma_a^1 T + \gamma_a^2 a + \gamma_a^3 \varepsilon_{kk}, \tag{52}$$

$$\overset{*}{\mathcal{V}}_k = \gamma_{\mathcal{V}}^1 a_{,k} + \gamma_{\mathcal{V}}^2 T_{,k} + \gamma_{\mathcal{V}}^3 \mathcal{V}_k + \gamma_{\mathcal{V}}^4 q_k, \tag{53}$$

$$\overset{*}{q}_k = \gamma_q^1 a_{,k} + \gamma_q^2 T_{,k} + \gamma_q^3 \mathcal{V}_k + \gamma_q^4 q_k, \tag{54}$$

where the coefficients γ_a^ε $(\varepsilon = 1, 2, 3)$, are functions depending on the invariants (49) and $\gamma_{\mathcal{V}}^\eta$, γ_q^η $(\eta = 1, 2, 3, 4)$ can depend on suitable invariants built on appropriate variables of the set C (6) (see [32]). In the case where we can use the material derivative instead of Zaremba-Jaumann derivative, Eqs. (52) - (54) can also be written in the form

$$\dot{a} + \mathcal{V}_{k,k} = \gamma_a^1 T + \gamma_a^2 a + \gamma_a^3 \varepsilon_{kk}, \tag{55}$$

$$\tau^{\mathcal{V}} \dot{\mathcal{V}}_k = -\mathcal{V}_k + \chi_{\mathcal{V}}^1 a_{,k} + \chi_{\mathcal{V}}^2 T_{,k} + \chi_{\mathcal{V}}^4 q_k. \tag{56}$$

$$\tau^q \dot{q}_k = -q_k + \chi_q^1 a_{,k} + \chi_q^2 T_{,k} + \chi_q^4 \mathcal{V}_k, \tag{57}$$

where $\tau^{\mathcal{V}}$ and τ^q are the relaxation times of the fields $\boldsymbol{\mathcal{V}}$ and $\mathbf{q}$, respectively, the new coefficients $\chi_{\mathcal{V}}^{(\varepsilon)}$ and $\chi_q^{(\varepsilon)}$ $(\varepsilon = 1, 2, 4)$, in (56) and (57), are expressed in terms of the coefficients present in equations (53) and (54) and the minus signs come from physical reasons. The rate equation (57) for the heat flux generalizes Vernotte-Cattaneo relation, where the finite velocity of the thermal disturbances is taken into consideration (eliminating the paradox of Fourier heat equation, that leads to thermal propagation with infinite velocity) [38], [39].

5 Conclusions

In this paper a model for nanocrystals with defects of dislocation was given in the framework of extended irreversible thermodynamics with internal variables. It was assumed that the media under consideration have constant mass density, the body force and heat source are negligible and the dislocation field (the internal variable), its flux and heat flux are independent variables in addition to the classical variables ε_{ij} and T. Also the non local effects of the temperature field and dislocation field were taken into account, introducing le variables $T_{,i}$ and $a_{ij,k}$. The entropy inequality was analyzed by Liu′s theorem, where all balance and evolution equations of the problem are considered as mathematical constraints for its validity and the state laws, the affinities, the residual inequality, the entropy flux and other relations were obtained. By the help of Smith's theorem constitutive theory and the rate equations for the dissipative fluxes and the dislocation field, formulated as ansatzes in the form of balance equations describing time-dependent fields, were formulated in a first approximation. It is seen that dislocation field in nanocrystals influence mechanical and transport properties. Then, the obtained results have several applications in nanotechnology and in other sectors of applied sciences.

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Appendix

In Eqs. (17), (19), (20) and $(21)_1$ the elements of the matrix $\{A_{\triangle\gamma}\} = \{A^{m/n}\}$ are the following:

$$A^{1/1} = \rho\delta_{ir}, \quad A^{1/2} = ... = A^{1/8} = 0, \quad A^{1/9} = \rho v_k \delta_{ir}, \quad A^{1/10} = -\frac{\partial \sigma_{kr}}{\partial \varepsilon_{ij}},$$

$$A^{1/11} = -\frac{\partial \sigma_{kr}}{\partial q_i}, \;\; A^{1/12} = -\frac{\partial \sigma_{kr}}{\partial \mathcal{V}_{ijp}}\delta_{kl}, \;\; A^{1/13} = -\frac{\partial \sigma_{kr}}{\partial T_{,i}}, \;\; A^{1/14} = -\frac{\partial \sigma_{kr}}{\partial a_{ij,p}}\delta_{kl},$$

$$A^{2/1}=0,\quad A^{2/2}=\rho\frac{\partial e}{\partial\varepsilon_{ij}},\quad A^{2/3}=\rho\frac{\partial e}{\partial T},\quad A^{2/4}=\rho\frac{\partial e}{\partial a_{ij}},$$

$$A^{2/5}=\rho\frac{\partial e}{\partial q_i},\quad A^{2/6}=\rho\frac{\partial e}{\partial\mathcal{V}_{ijp}},\quad A^{2/7}=\rho\frac{\partial e}{\partial T_{,i}},\quad A^{2/8}=\rho\frac{\partial e}{\partial a_{ij,p}},$$

$$A^{2/9}=-\sigma_{ji}\delta_{jk},\quad A^{2/10}=\rho v_k\frac{\partial e}{\partial\varepsilon_{ij}},\quad A^{2/11}=\rho v_k\frac{\partial e}{\partial q_i}+\delta_{ik},$$

$$A^{2/12}=\rho v_k\frac{\partial e}{\partial\mathcal{V}_{ijp}}\delta_{kl},\quad A^{2/13}=\rho v_k\frac{\partial e}{\partial T_{,i}},\quad A^{2/14}=\rho v_k\frac{\partial e}{\partial r_{ij,p}}\delta_{kl}$$

$$A^{3/1}=0,\quad A^{3/2}=r_{sr}\delta_{mi}\delta_{js}+r_{ms}\delta_{ir}\delta_{js},\quad A^{3/3}=0,\quad A^{3/4}=\delta_{im}\delta_{jr},$$

$$A^{3/5}=...=A^{3/8}=0,\quad A^{3/9}=-r_{sr}\delta_{mi}\delta_{js}-r_{ms}\delta_{ir}\delta_{js},$$

$$A^{3/10}=A^{3/11}=0,\quad A^{3/12}=\delta_{im}\delta_{jr}\delta_{pl},\quad A^{3/13}=A^{3/14}=0,$$

$$A^{4/1}=0,\quad A^{4/2}=q_k\delta_{kj},\quad A^{4/3}=A^{4/4}=0,\quad A^{4/5}=1,$$

$$A^{4/6}=...=A^{4/8}=0,\quad A^{4/9}=-q_k,\quad A^{4/10}=0,$$

$$A^{4/11}=v_k,\quad A^{4/12}=...=A^{4/14}=0,$$

$$A^{5/1}=0,\quad A^{5/2}=\mathcal{V}_{srp}\delta_{mi}\delta_{sj}+\mathcal{V}_{msp}\delta_{ri}\delta_{sj}+\mathcal{V}_{mrs}\delta_{pi}\delta_{sj},$$

$$A^{5/3}=...=A^{5/5}=0,\quad A^{5/6}=\delta_{im}\delta_{rj}\quad A^{5/7}=A^{5/8}=0,$$

$$A^{5/9}=-\mathcal{V}_{srp}\delta_{mi}\delta_{sj}-\mathcal{V}_{msp}\delta_{ri}\delta_{sj}-\mathcal{V}_{mrs}\delta_{pi}\delta_{sj},$$

$$A^{5/10}=A^{5/11}=0,\quad A^{7/12}=v_s\delta_{im}\delta_{rj}\delta_{sl},\quad A^{5/13}=A^{5/14}=0. \tag{58}$$

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