

A DESCRIPTION OF ANISOTROPIC POROUS NANOCRYSTALS FILLED BY A FLUID FLOW IN THE FRAMEWORK OF EXTENDED THERMODYNAMICS WITH INTERNAL VARIABLES

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Abstract. In a previous paper a non conventional model for fluid-saturated porous nanocrystals was derived in the framework of non-equilibrium thermodynamics introducing in the thermodynamic state vector, as internal variables describing the porous tubes, a structural permeability tensor λ la Kubik, r_{ij} , its gradient, $r_{ij,k}$, and its flux, \mathcal{V}_{ijk} . Here, we work out for nanocrystals with porous channels filled by fluid flow, in the anisotropic and linear case, the constitutive relations for the stress tensor, the entropy density, the chemical potentials for the concentration of the fluid and for the porosity field, and the rate equations for r_{ij} , \mathcal{V}_{ijk} , the fluid-concentration and the heat fluxes, describing disturbances propagating with finite velocity. Also, the closure of the system of equations describing the behaviour of these nanosystems is discussed, presenting the linearized temperature and internal energy equations. The obtained results may have relevance in important advanced studies on nanostructures, where their porous defects have a direct influence on mechanical and transport properties, in particular on thermal conductivity. Inside these nanomaterials there are situations of high-frequency waves propagation and the phenomena are fast.

Key words: non-equilibrium thermodynamics, internal variables, porous media, constitutive relations.

1. INTRODUCTION

The description of phenomena accompanying flows of mass in porous structures finds applications in materials science, such as in miniaturized systems, and also in medical sciences, biology and geology. Here, we use a thermodynamic approach based on the extended irreversible thermodynamics (see [1–8]). The influence of porous channels on the other fields occurring inside nanocrystals is illustrated by the introduction of a structural permeability tensor λ la Kubik [9] (see also [10]), giving a macroscopic geometrical characterization of a porous structure, coming from the use of volume and area averaging procedures at microscopic level. Models for porous media, with some applications, were developed in [11–15]. In this paper, using the model formulated in [11] (see also [12]), we consider the anisotropic case. Porous channels modify the thermal conductivity. Understanding their influence on mechanical and transport properties in miniaturized systems is an interesting topic in “defect engineering”, because by experimental and theoretical studies it was found that the porous density has a minor effect on the thermal conductivity for porous defects densities smaller than a characteristic value dependent on the material and temperature, but for higher values, the thermal conductivity decreases, and this situation influences the nanodevice performances. Nanostructures can present metallurgical defects (for example porous channels, inclusions, cavities, microfissures, dislocations), that sometimes can self propagate because of some conditions and surrounding conditions that are favorable. A relatively high temperature gradient could produce, for instance, a migration of defects inside the system. In [16–25], models, with some applications for media with defects such as piezoelectric, elastic, semiconductor and superlattice structures, were also formulated using the methods of non-equilibrium thermodynamics and introducing an internal variable, its gradient and its flux, describing the defects inside the media under consideration. In [26–30] non-equilibrium temperatures and

heat equation were studied in media with internal variables, in the framework of non-equilibrium thermodynamics. In this paper we describe the behaviour of nanocrystals with defects, where the rate of variation of the properties of the system is faster than the time scale characterizing the relaxation of the fluxes towards their respective local-equilibrium value. In these nanosystems, there are situations of high-frequency waves propagation. Then, in extended thermodynamics it is essential to incorporate the fluxes among the state variables. Micro- and nanomaterials are characterized by the property that their volume element size L along some directions is so small that it becomes comparable (or smaller than) the free mean path l of the heat carriers (representing the average distance traveled by the phonons between two successive collisions), i.e. $L \leq l$. Then, at this scale the Knudsen number $\frac{l}{L}$ is such that $\frac{l}{L} \geq 1$ (see [26] and [31]). In Sections 2 and 3 in the frame of extended irreversible thermodynamics with internal variables, a model formulated in [11] is presented for media with porous channels filled by fluid flow, where the geometrical internal structure is described by a structural permeability tensor [9], its gradient and its flux. The very thin porous tubes can self propagate and influence mechanical and transport properties of these porous media. In Sections 4, 5 and 6 in the anisotropic and linear case, the constitutive theory is derived, developing the free energy around a particular thermodynamic equilibrium state, and the rate equations for the structural permeability tensor, its flux, the heat and the fluid fluxes are worked out, describing disturbances with finite velocity and fast phenomena. According to the extended thermodynamics generalized Maxwell-Cattaneo-Vernotte and Fick-Nonnenmacher transport equations for the heat and fluid fluxes, respectively, are derived, from which it is seen the influence of the porous channels on the transport properties of the medium. Finally, the closure of the system of equations describing the behaviour of these media is discussed, presenting the linearized temperature and internal energy equations. The obtained results have a technological interest in the production of very miniaturized systems (nanotechnology) and the study of high-frequency processes.

2. A MODEL FOR POROUS NANOCRYSTALS

In this section, we present a model for fluid-saturated porous nanocrystals, developed in [11], in the framework of extended irreversible thermodynamics with internal variables, where, among the various descriptions of porous structures, that one based on the consideration of a structural permeability tensor r_{ij} à la Kubik [9] is used, and the tensor r_{ij} , its gradient and its flux are introduced in the thermodynamic state vector (see [10]).

The tensor r_{ij} is symmetric and describes a structure of very thin porous channels inside the medium under consideration [9]. To describe as the porosity field evolves (see [11]), we introduce in the thermodynamic state vector the structural permeability field r_{ij} , its gradient $r_{ij,k}$ and its flux \mathcal{V}_{ijk} . We assume that the mass of the fluid filling the porous channels inside the crystal and the same crystal form a two-components mixture. We indicate by ρ_1 the mass of the fluid transported through the elastic porous solid of density ρ_2 . Furthermore, the fluid flow is described by two variables: the concentration of the fluid $c = \frac{\rho_1}{\rho}$, its gradient $c_{,i}$ and its flux j_i^c . Thus, we have the following expression: $\rho = \rho_1 + \rho_2$. For the mixture of continua as a whole and also for each constituent the following continuity equations are satisfied: $\dot{\rho} + \rho v_{i,i} = 0$, $\frac{\partial \rho_1}{\partial t} + (\rho_1 v_{1i})_{,i} = h_1$, $\frac{\partial \rho_2}{\partial t} + (\rho_2 v_{2i})_{,i} = h_2$, where a superimposed dot denotes the material derivative, h_1 and h_2 are the source terms, that in the following are not taken into consideration, v_{1i} and v_{2i} are the velocities of the fluid particles and the particles of the elastic body, respectively. We introduce the barycentric velocity and the fluid-concentration flux as follows: $\rho v_i = \rho_1 v_{1i} + \rho_2 v_{2i}$, $j_i^c = \rho_1 (v_{1i} - v_i)$. The thermal field is described by the temperature T , its gradient $T_{,i}$ and the heat flux q_i . The mechanical field is described by the symmetric total stress tensor τ_{ij} , referred to the whole system considered as a mixture, and by the small strain tensor $\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$, being \mathbf{u} the displacement vector. We choose the following

$$\text{thermodynamic vector space} \quad C = \{\varepsilon_{ij}, c, T, r_{ij}, j_i^c, q_i, \mathcal{V}_{ijk}, c_{,i}, T_{,i}, r_{ij,k}\}, \quad (1)$$

where we have ignored the viscous effects. The processes occurring inside the considered nanocrystals are governed by two sets of laws. The first set deals with the classical *balance equations* (the *balance of mass*, the *momentum balance* and the *internal energy balance*), having, respectively, the following form:

$$\rho \dot{c} + j_{i,i}^c = 0, \quad \rho \dot{v}_i - \tau_{ji,j} - f_i = 0, \quad \rho \dot{e} - \tau_{ji} v_{i,j} + q_{i,i} - \rho h = 0, \quad (2)$$

where f_i denotes a body force, e is the internal energy density, h is the energy source density, and $v_{i,j}$ is the gradient of the velocity of the body, given by $v_{i,j} = w_{ij} + \frac{d\varepsilon_{ij}}{dt}$, with $w_{ij} = \frac{1}{2}(v_{i,j} - v_{j,i})$ the antisymmetric part of $v_{i,j}$ and $\frac{d\varepsilon_{ij}}{dt} = \frac{1}{2}(v_{i,j} + v_{j,i})$ the symmetric part. In the following f_i and h will be neglected.

The second set of laws concerns the *evolution equations* of the structural permeability field r_{ij} , its flux \mathcal{V}_{ijk} , the fluid-concentration flux j_i^c and the heat flux q_i . These rate equations are constructed obeying the objectivity and frame-indifference principles (see [32], [33] and [34]). Thus, these *rate equations* are chosen having the form

$$r_{ij}^* + \mathcal{V}_{ijk,k} - \mathcal{R}_{ij}(C) = 0, \quad j_i^c - J_i^c(C) = 0, \quad q_i - Q_i(C) = 0, \quad \mathcal{V}_{ijk} - V_{ijk}(C) = 0, \quad (3)$$

where the symbol (*) denotes the Zaremba-Jaumann derivative defined for a general rank tensor as follows $a_{ij\dots m}^* = \dot{a}_{ij\dots m} - w_{ip}a_{pj\dots m} - w_{jp}a_{ip\dots m} - \dots - w_{mp}a_{ij\dots p}$, $\mathcal{R}_{ij}(C)$ is the source-like term dealing with the creation or annihilation of porous channels, $J_i^c(C)$ is the fluid-concentration flux source, $Q_i(C)$ is the heat flux source and $V_{ijk}(C)$ is the source term for the structural permeability field flux. \mathcal{R}_{ij} , J_i^c , Q_i and V_{ijk} are constitutive functions of the independent variables (see (1)). In (3) the flux terms of r_{ij} , j_i^c , q_i and \mathcal{V}_{ijk} are not present, in order to close the system of equations describing the considered media, and the expression $w_{ij} = v_{i,j} - \frac{\partial \varepsilon_{ij}}{\partial t}$ is used to obtain linear relations.

3. ANALYSIS OF ENTROPY PRODUCTION

For the purpose that our investigations concern real physical processes occurring in the considered porous structure filled by a fluid flow, all the admissible solutions of the proposed evolution equations should be restricted by the following entropy inequality $\rho \dot{S} + \phi_{i,i} - \frac{\rho h}{T} = \sigma^{(s)} \geq 0$, where S is the entropy density, $\sigma^{(s)}$ is the internal entropy production, ϕ_i is the entropy flux and $\frac{\rho h}{T}$ is the external entropy production source, that will be neglected in the sequel. Furthermore, the total mass density ρ of the considered nanocrystals is supposed constant. Let us consider the following set of constitutive functions (dependent functions on the set (1)): $W = \{\tau_{ij}, e, \mathcal{R}_{ij}, J_i^c, Q_i, V_{ijk}, S, \phi_i, \Pi^c, \Pi_{ij}^r, \Pi_i^c, \Pi_i^q, \Pi_{ijk}^v\}$ (with Π^c the chemical potential of the fluid concentration field, Π_{ij}^r a potential related to the structural permeability field and $\Pi_i^c, \Pi_i^q, \Pi_{ijk}^v$ the generalized affinities conjugated to the respective fluxes j_i^c, q_i and \mathcal{V}_{ijk}), having the general form $W = \bar{W}(C)$, where both C and W are evaluated at the same point and time. In [11] Liu's theorem [35], that considers all balance and evolution equations as mathematical constraints for the general validity of the entropy inequality, was applied, and the following results and some others were obtained, introducing the free energy density $F = e - Ts$ and the flux vector $K_k = \rho F v_k - T \phi_k$:

• *the state laws* (defining the constitutive functions via the partial derivatives of the free energy with respect to the respective conjugate variables):

$$\tau_{ij} = \rho \frac{\partial F}{\partial \varepsilon_{ij}}, \quad S = -\frac{\partial F}{\partial T}, \quad \Pi^c = \frac{\partial F}{\partial c}, \quad \Pi_{ij}^r = \rho \frac{\partial F}{\partial r_{ij}}, \quad \frac{\partial F}{\partial c_{,i}} = 0, \quad \frac{\partial F}{\partial T_{,i}} = 0, \quad \frac{\partial F}{\partial r_{ij,k}} = 0; \quad (4)$$

$$\text{- the generalized affinities:} \quad \Pi_i^c = \rho \frac{\partial F}{\partial j_i^c}, \quad \Pi_i^q = \rho \frac{\partial F}{\partial q_i}, \quad \Pi_{ijk}^v = \rho \frac{\partial F}{\partial \mathcal{V}_{ijk}}; \quad (5)$$

$$\text{- the residual inequality} \quad T \frac{\partial \phi_i}{\partial c_{,i}} + T \frac{\partial \phi_i}{\partial T} T_{,i} + T \frac{\partial \phi_i}{\partial r_{jk,i}} r_{jk,i} - \Pi_{ij}^r \mathcal{R}_{ij} - \Pi_i^c J_i^c - \Pi_i^q Q_i - \Pi_{ijk}^v V_{ijk} \geq 0; \quad (6)$$

the *entropy flux* $\phi_k = \frac{1}{T}(q_k - \Pi^c j_k^c - \Pi_{ij}^r \mathcal{V}_{ijk})$, the form for the free energy F as $F = F(\varepsilon_{ij}, c, T, r_{ij}, j_i^c, q_i, \mathcal{V}_{ijk})$, and the symmetry for the stress tensor τ_{ij} (see (4)₁).

4. CONSTITUTIVE RELATIONS AND GENERALIZED AFFINITIES

In this Section, we derive in the anisotropic case and in the linear approximation the constitutive theory for the system under consideration. We recall that the total mass density ρ has been assumed to be constant. We apply the potential method and we expand the free energy $F(\varepsilon_{ij}, c, T, r_{ij}, j_i^c, q_i, \mathcal{V}_{ijk})$ up the second-order approximation around a thermodynamic equilibrium state indicated by “0”. Introducing the deviations of the independent variables from this reference state, in particular: $\theta = T - T_0$, with $\left|\frac{\theta}{T_0}\right| \ll 1$, $\tilde{e} = e - e_0$, with $\left|\frac{\tilde{e}}{e_0}\right| \ll 1$, $\mathcal{C} = c - c_0$, with $\left|\frac{\mathcal{C}}{c_0}\right| \ll 1$, $\mathcal{S} = S - S_0$, with $\left|\frac{\mathcal{S}}{S_0}\right| \ll 1$, $R_{ij} = r_{ij} - r_{0ij}$, with $\left|\frac{R_{ij}}{r_{0ij}}\right| \ll 1$,

$$\text{assuming} \quad (\varepsilon_{ij})_0 = 0, \quad (\tau_{ij})_0 = 0, \quad (r_{ij})_0 = r_{0ij}, \quad (u_i)_0 = u_{0i}, \quad (v_i)_0 = v_{0i}, \quad (7)$$

and taking into account that

$$(\mathcal{V}_{ijk})_0 = 0, \quad (q_i)_0 = 0, \quad (j_i^c)_0 = 0, \quad (\Pi_{ij}^c)_0 = 0, \quad (\Pi^c)_0 = 0, \quad (\Pi_{ijk}^v)_0 = 0, \quad (\Pi_i^j)_0 = 0, \quad (\Pi_i^q)_0 = 0, \quad (8)$$

we obtain

$$\begin{aligned} F = F_0 - S_0\theta + \frac{1}{2\rho} c_{ijkl} \varepsilon_{ij} \varepsilon_{lm} - \frac{\lambda_{ij}^{\theta\varepsilon}}{\rho} \theta \varepsilon_{ij} + \frac{\lambda_{ijlm}^{r\varepsilon}}{\rho} \varepsilon_{ij} R_{lm} - \frac{\lambda_{ij}^{c\varepsilon}}{\rho} \mathcal{C} \varepsilon_{ij} - \frac{1}{2} c_v \theta^2 + \frac{\lambda_{ij}^{r\theta}}{\rho} R_{ij} \theta + \frac{\lambda^{\theta c}}{\rho} \theta \mathcal{C} + \frac{\lambda_{ij}^{rc}}{\rho} R_{ij} \mathcal{C} \\ + \frac{\lambda_{ijlm}^{rr}}{2\rho} R_{ij} R_{lm} + \frac{\lambda^c}{2\rho} \mathcal{C}^2 + \frac{\lambda_{ijklmn}^{vv}}{2\rho} \mathcal{V}_{ijk} \mathcal{V}_{lmn} + \frac{\lambda_{ijkl}^{vj^c}}{\rho} \mathcal{V}_{ijk} j_l^c + \frac{\lambda_{ijkl}^{vq}}{\rho} \mathcal{V}_{ijk} q_l + \frac{1}{2\rho} \lambda_{ij}^{qq} q_i q_j + \frac{1}{2\rho} \lambda_{ij}^{j^c j^c} j_i^c j_j^c + \frac{1}{\rho} \lambda_{ij}^{j^c q} j_i^c q_j, \end{aligned} \quad (9)$$

where $c_{ijkl} = \rho \left(\frac{\partial^2 F}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} \right)_0$, $\lambda^c = \rho \left(\frac{\partial^2 F}{\partial c^2} \right)_0$, $c_v = -T_0 \left(\frac{\partial^2 F}{\partial T^2} \right)_0$, $\lambda^{j^c j^c} = \rho \left(\frac{\partial^2 F}{\partial j_i^c \partial j_k^c} \right)_0$, $\lambda_{ij}^{\theta\varepsilon} = -\rho \left(\frac{\partial^2 F}{\partial \varepsilon_{ij} \partial T} \right)_0$, $\lambda_{ijklmn}^{vv} = \rho \left(\frac{\partial^2 F}{\partial \mathcal{V}_{ijk} \partial \mathcal{V}_{lmn}} \right)_0$, $\lambda_{ijkl}^{vj^c} = \rho \left(\frac{\partial^2 F}{\partial q_i \partial \mathcal{V}_{jkl}} \right)_0$, $\lambda_{ijkl}^{r\varepsilon} = \rho \left(\frac{\partial^2 F}{\partial r_{ij} \partial r_{kl}} \right)_0$, $\lambda^{\theta c} = \rho \left(\frac{\partial^2 F}{\partial c \partial T} \right)_0$, $\lambda_{ij}^{rc} = \rho \left(\frac{\partial^2 F}{\partial c \partial r_{ij}} \right)_0$, $\lambda_{ij}^{qq} = \rho \left(\frac{\partial^2 F}{\partial q_i \partial q_j} \right)_0$, $\lambda_{ij}^{c\varepsilon} = -\rho \left(\frac{\partial^2 F}{\partial \varepsilon_{ij} \partial c} \right)_0$, $\lambda_{ik}^{j^c q} = \rho \left(\frac{\partial^2 F}{\partial j_i^c \partial q_k} \right)_0$, $\lambda_{ij}^{r\theta} = \rho \left(\frac{\partial^2 F}{\partial T \partial r_{ij}} \right)_0$, $\lambda_{ijkl}^{r\varepsilon} = \rho \left(\frac{\partial^2 F}{\partial \varepsilon_{ij} \partial r_{kl}} \right)_0$, $\lambda_{ijkl}^{vj^c} = \rho \left(\frac{\partial^2 F}{\partial j_i^c \partial \mathcal{V}_{jkl}} \right)_0$.

In (9) we have called the second partial derivatives of free energy with respect to the considered independent variables using the name of the phenomenological coefficients, measurable by experiments, coming from their physical interpretation. In (9) c_v denotes the specific heat, c_{ijkl} is the elastic tensor, $\lambda_{ij}^{\theta\varepsilon}$ are the thermoelastic constants and the other phenomenological coefficients express simple and coupled effects which can manifest among the fields themselves or the different fields acting during interactions. Also, we have taken into consideration the physical dimensions of the physical quantities and the invariance of F under time reversal, so that the terms containing the fluxes at first order are null. Furthermore, the introduction of the minus sign comes from physical reasons and the constant phenomenological coefficients satisfy the following symmetric relations (because they are defined in terms of second derivatives of F and the tensors ε_{ij} and r_{ij} are symmetric):

$$\begin{aligned} c_{ijkl} = c_{lmij} = c_{jilm} = c_{ijml} = c_{jmil} = c_{mlij} = c_{mlji} = c_{lmji}, \quad \lambda_{ij}^{c\varepsilon} = \lambda_{ji}^{c\varepsilon}, \quad \lambda_{ij}^{r\theta} = \lambda_{ji}^{r\theta}, \quad \lambda_{ij}^{vj^c} = \lambda_{ji}^{vj^c}, \\ \lambda_{ijlm}^{r\varepsilon} = \lambda_{lmji}^{r\varepsilon} = \lambda_{lmij}^{r\varepsilon} = \lambda_{jilm}^{r\varepsilon} = \lambda_{ijml}^{r\varepsilon} = \lambda_{jmil}^{r\varepsilon} = \lambda_{mlji}^{r\varepsilon} = \lambda_{mlij}^{r\varepsilon}, \quad \lambda_{ij}^{qq} = \lambda_{ji}^{qq}, \quad \lambda_{ij}^{rc} = \lambda_{ji}^{rc}, \quad \lambda_{ij}^{j^c q} = \lambda_{ji}^{j^c q}, \quad \lambda_{ij}^{j^c j^c} = \lambda_{ji}^{j^c j^c}, \\ \lambda_{ijlm}^{rr} = \lambda_{lmij}^{rr} = \lambda_{ijml}^{rr} = \lambda_{jilm}^{rr} = \lambda_{jmil}^{rr} = \lambda_{mlji}^{rr} = \lambda_{mlij}^{rr}, \quad \lambda_{ij}^{\theta\varepsilon} = \lambda_{ji}^{\theta\varepsilon}, \quad \lambda_{ijklmn}^{vv} = \lambda_{lmnijk}^{vv}, \quad \lambda_{ijkl}^{vq} = \lambda_{l_ijk}^{vq}. \end{aligned}$$

From (9), using equations (4) and (5), we obtain the *constitutive functions* τ_{ij} , S , Π_{ij}^c , Π^c and the *generalized affinities* $\Pi_{ijk}^{\mathcal{V}}$, Π_i^q , $\Pi_i^{j^c}$:

$$\tau_{ij} = c_{ijklm} \varepsilon_{lm} - \lambda_{ij}^{\theta \varepsilon} \theta + \lambda_{ijlm}^{r \varepsilon} R_{lm} - \lambda_{ij}^{c \varepsilon} \mathcal{C}, \quad S = S_0 + \frac{\lambda_{ij}^{\theta \varepsilon}}{\rho} \varepsilon_{ij} + \frac{c_v}{T_0} \theta - \frac{\lambda_{ij}^{r \theta}}{\rho} R_{ij} - \frac{\lambda^{\theta c}}{\rho} \mathcal{C}, \quad (10)$$

$$\Pi_{ij}^r = \lambda_{ijlm}^{r \varepsilon} \varepsilon_{lm} + \lambda_{ij}^{r \theta} \theta + \lambda_{ijlm}^{rr} R_{lm} + \lambda_{ij}^{rc} \mathcal{C}, \quad \Pi^c = -\frac{\lambda_{ij}^{c \varepsilon}}{\rho} \varepsilon_{ij} + \frac{\lambda^{\theta c}}{\rho} \theta + \frac{\lambda_{ij}^{rc}}{\rho} R_{ij} + \frac{\lambda^c}{\rho} \mathcal{C}, \quad (11)$$

$$\Pi_{ijk}^{\mathcal{V}} = \lambda_{ijklmn}^{\mathcal{V}\mathcal{V}} \mathcal{V}_{lmn} + \lambda_{ijkl}^{\mathcal{V}q} q_l + \lambda_{ijkl}^{\mathcal{V}j^c} j_l^c, \quad \Pi_i^q = \lambda_{ijkl}^{\mathcal{V}q} \mathcal{V}_{jkl} + \lambda_{ij}^{qq} q_j + \lambda_{ij}^{qj^c} j_j^c, \quad \Pi_i^{j^c} = \lambda_{ijkl}^{\mathcal{V}j^c} \mathcal{V}_{jkl} + \lambda_{ij}^{j^c q} q_j + \lambda_{ij}^{j^c j^c} j_j^c. \quad (12)$$

5. RATE EQUATIONS

The residual inequality (6) imposes some relations among the source terms \mathcal{R}_{ij} , J_i^c , Q_i , V_{ijk} and Π_{ij}^r , $\Pi_i^{j^c}$, Π_i^q and $\Pi_{ijk}^{\mathcal{V}}$, respectively. In this Section we work out the rate equations for the heat and fluid fluxes for the structural permeability tensor and its flux. In particular, expressing the source terms \mathcal{R}_{ij} , J_i^c , Q_i and V_{ijk} as linear polynomials with constant coefficients in terms of the independent variables, and in the case where we may use the material derivative instead of Zaremba-Jaumann derivative we obtain

$$\dot{q}_i = \alpha_{ij}^1 j_j^c + \alpha_{ij}^2 q_j + \alpha_{ijkl}^3 \mathcal{V}_{jkl} + \alpha_{ij}^4 c_{,j} + \alpha_{ij}^5 T_{,j} + \alpha_{ijkl}^6 r_{jk,l}, \quad (13)$$

$$\dot{j}_i^c = \eta_{ij}^1 j_j^c + \eta_{ij}^2 q_j + \eta_{ijkl}^3 \mathcal{V}_{jkl} + \eta_{ij}^4 c_{,j} + \eta_{ij}^5 T_{,j} + \eta_{ijkl}^6 r_{jk,l}, \quad (14)$$

$$\dot{r}_{ij} + \mathcal{V}_{ijk,k} = \beta_{ijkl}^1 \varepsilon_{kl} + \beta_{ijkl}^2 r_{kl} + \beta_{ijk}^3 j_k^c + \beta_{ijk}^4 q_k + \beta_{ijklm}^5 \mathcal{V}_{klm} + \beta_{ijk}^6 c_{,k} + \beta_{ijk}^7 T_{,k} + \beta_{ijklm}^8 r_{kl,m}, \quad (15)$$

$$\dot{\mathcal{V}}_{ijk} = \gamma_{ijkl}^1 j_l^c + \gamma_{ijkl}^2 q_l + \gamma_{ijklmn}^3 \mathcal{V}_{lmn} + \gamma_{ijkl}^4 c_{,l} + \gamma_{ijkl}^5 T_{,l} + \gamma_{ijklmn}^6 r_{lm,n}. \quad (16)$$

Equations (13)-(16) contain coupled effects among the different fields and describe propagation of disturbances with finite velocity, following the philosophy of extended thermodynamics. In these rate equations the fields q_i , j_i^c , r_{ij} and \mathcal{V}_{ijk} present a relaxation time. The rate equation (13) for the heat flux generalizes Maxwell-Vernotte-Cattaneo relation for the thermal disturbances with finite velocity and denoting by τ_{ij}^q a relaxation times tensor associated to the heat flux, it takes the form

$$\tau_{ij}^q \dot{q}_j = \chi_{ij}^1 j_j^c - q_i + \chi_{ijkl}^3 \mathcal{V}_{jkl} + \chi_{ij}^4 c_{,j} - \chi_{ij}^5 T_{,j} + \chi_{ijkl}^6 r_{jk,l}. \quad (17)$$

In (17) we have used the following notations $\chi_{ik}^1 = \tau_{ij}^q \alpha_{jk}^1$, $\delta_{ik} = -\tau_{ij}^q \alpha_{jk}^2$, $\chi_{iklm}^3 = \tau_{ij}^q \alpha_{jklm}^3$, $\chi_{ik}^4 = \tau_{ij}^q \alpha_{jk}^4$, $\chi_{ik}^5 = -\tau_{ij}^q \alpha_{jk}^5$, $\chi_{iklm}^6 = \tau_{ij}^q \alpha_{jklm}^6$, where χ_{ij}^1 is the thermodiffusive kinetic tensor, χ_{ij}^4 is the thermodiffusive tensor and χ_{ij}^5 is the heat conductivity tensor.

$$\text{Equation (17) becomes } \tau^q \dot{q}_i + q_i = \chi_{ij}^1 j_j^c + \chi_{ijkl}^3 \mathcal{V}_{jkl} + \chi_{ij}^4 c_{,j} - \chi_{ij}^5 T_{,j} + \chi_{ijkl}^6 r_{jk,l} \quad \text{when } \tau_{ij}^q = \tau^q \delta_{ij}. \quad (18)$$

In the case where the coefficients χ^s ($s = 1, 3, 4, 6$) are negligible, equation (17) has the form

$$\tau_{ij}^q \dot{q}_j + q_i = -\chi_{ij}^5 T_{,j}, \quad (19)$$

that is the anisotropic Maxwell-Cattaneo-Vernotte equation. In the isotropic case $\chi_{ij}^5 = \chi \delta_{ij}$ and $\tau_{ij}^q = \tau^q \delta_{ij}$ and we obtain the well known Maxwell-Cattaneo equation $\tau^q \dot{q}_j + q_i = -\chi T_{,i}$. When the thermal propagation has infinite velocity, equation (19) becomes the anisotropic Fourier law $q_i = -\chi_{ij}^5 T_{,j}$, having in the isotropic case the classical form $q_i = -\chi T_{,i}$, with χ the thermal conductivity.

Furthermore, the rate equation (14) for the fluid flux generalizes the Fick-Nonnenmacher law, that, introducing the fluid flux relaxation time tensor $\tau_{ij}^{j^c}$, has the form

$$\tau_{ij}^{j^c} \dot{j}_j^c = -j_i^c + \xi_{ij}^2 q_j + \xi_{ijkl}^3 \mathcal{V}_{jkl} - \xi_{ij}^4 c_{,j} + \xi_{ij}^5 T_{,j} + \xi_{ijkl}^6 r_{jk,l}, \quad (20)$$

where $\delta_{ik} = -\tau_{ij}^j \eta_{jk}^1$, $\xi_{ik}^2 = \tau_{ij}^j \eta_{jk}^2$, $\xi_{iklm}^3 = \tau_{ij}^j \eta_{jklm}^3$, $\xi_{ik}^4 = -\tau_{ij}^j \eta_{jk}^4$, $\xi_{ik}^5 = \tau_{ij}^j \eta_{jk}^5$, $\xi_{iklm}^6 = \tau_{ij}^j \eta_{jklm}^6$. The quantities ξ_{ik}^4 and ξ_{ik}^5 are the diffusion tensor and the thermodiffusive tensor, respectively. In the case where the coefficients ξ_{ij}^2 , ξ_{ijkl}^3 , ξ_{ij}^5 and ξ_{ijkl}^6 are null equation (20) represents the anisotropic Fick-Nonnenmacher law.

Equation (20) becomes $\tau^{jc} \dot{j}_i + j_i^c = \xi_{ij}^2 q_j + \xi_{ijkl}^3 \mathcal{V}_{jkl} - \xi_{ij}^4 c_{,j} + \xi_{ij}^5 T_{,j} + \xi_{ijkl}^6 r_{jk,l}$, when $\tau_{ij}^j = \tau^j \delta_{ij}$. (21)

6. LINEARIZED TEMPERATURE EQUATION AND BALANCE INTERNAL ENERGY EQUATION

In [10], starting from the free energy $F = e - TS$, calculating its material derivative and taking into consideration the balance energy equation $\rho \dot{e} = \tau_{ij} \dot{\varepsilon}_{ij} - q_{i,i}$ (where the expression for the velocity gradient $v_{i,j} = \dot{\varepsilon}_{ij} + w_{ij}$ has been used), we have deduced $\rho T \dot{S} = \tau_{ij} \dot{\varepsilon}_{ij} - q_{i,i} - \rho \dot{T} S - \rho \dot{F}$. Furthermore, expliciting the material derivative of the free energy F in terms of its independent variables, using the state laws (4), the definitions of the affinities (5), and linearizing the equation around the equilibrium state defined by (7) and (8) we have obtained $\rho(T_0 + \theta)(\dot{S}_0 + \dot{\mathcal{S}}) = -q_{i,i} - \Pi_{ij}^r [(\dot{r}_{0ij}) + \dot{R}_{ij}] - \Pi^c (\dot{c}_0 + \dot{\mathcal{C}}) - \Pi_{ijk}^{\mathcal{V}} \dot{\mathcal{V}}_{ijk} - \Pi_i^{jc} \dot{j}_i^c - \Pi_i^q \dot{q}_i$, and than

$$\rho T_0 \dot{S} = -q_{i,i}, \quad \tau^q \rho T_0 \dot{S} = -\tau^q \dot{q}_{i,i}, \quad (22)$$

where second order infinitesimal terms have been neglected. In (22) the superimposed dot indicates the linearized time derivative $\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v}_0 \cdot \text{grad}$ and the deviations of the fields from the thermodynamic equilibrium state have been indicated by the same symbols of the fields themselves. Furthermore, in (22) we have used the rate equation (18) for the heat flux linearized around the considered equilibrium state and, from equations (10)₂, (18) and (22)₂, we have deduced

$$\tau^q \dot{T} + \dot{T} = k_{ij} T_{,ij} - \gamma_{ij} (\tau^q \dot{\varepsilon}_{ij} + \dot{\varepsilon}_{ij}) + \varphi (\tau^q \dot{c} + \dot{c}) + \eta_{ij} (\tau^q \dot{r}_{ij} + \dot{r}_{ij}) - v_{ij}^1 j_{j,i}^c - v_{ijkl}^3 \mathcal{V}_{jkl,i} - v_{ijc}^4 c_{,ji} - v_{ijkl}^6 r_{jk,li}, \quad (23)$$

where $v_{ij}^1 = \frac{\chi_{ij}^1}{\rho c_v}$, $v_{ijkl}^3 = \frac{\chi_{ijkl}^3}{\rho c_v}$, $v_{ij}^4 = \frac{\chi_{ij}^4}{\rho c_v}$, $v_{ijkl}^6 = \frac{\chi_{ijkl}^6}{\rho c_v}$, $k_{ij} = \frac{\chi_{ij}^5}{\rho c_v}$, $\gamma_{ij} = \frac{T_0}{\rho c_v} \lambda_{ij}^{\theta \varepsilon}$, $\varphi = \frac{T_0}{c_v} \lambda^{\theta c}$, $\eta_{ij} = \frac{T_0}{\rho c_v} \lambda_{ij}^{r \theta}$, that generalizes the telegraph equation in the anisotropic case.

Here, we linearize the first law of thermodynamics. From (22)₁, using the relations $\bar{e} = e - e_0$, and (10)₂, considering the case where we may replace the material derivative by the partial time derivative, we obtain

$$\rho \dot{e} + T_0 \lambda_{ij}^{\theta \varepsilon} \dot{\varepsilon}_{i,j} + \rho c_v \dot{\theta} - T_0 \lambda_{ij}^{r \theta} \dot{r}_{ij} - T_0 \lambda^{\theta c} \dot{c} = 0, \quad \text{i.e.} \quad \rho \dot{e} = -T_0 \lambda_{ij}^{\theta \varepsilon} \dot{u}_{i,j} - \rho c_v \dot{T} + T_0 \lambda_{ij}^{r \theta} \dot{r}_{ij} + T_0 \lambda^{\theta c} \dot{c}. \quad (24)$$

In (24) the second order term $\tau_{ij} v_{i,j}$ has been neglected. Linearizing around the equilibrium state (see (7) and (8)), the balance equations (2)₁ and (2)₂ (where we insert the constitutive equations (10)₁), the rate equations (15), (16), (18) and (21), taking into account the linearized temperature equation (23) and the linearized internal energy balance equation (24)₂, and using the definitions of ε_{ij} and $v_i = \dot{u}_i$, we obtain a closed system of 45 equations for 45 unknowns: 1 for c , 3 for u_i , 1 for T , 1 for e , 6 for r_{ij} , 27 for \mathcal{V}_{ijk} , 3 for q_i and 3 for j_i^c .

7. CONCLUSIONS

In this article a model for porous nanocrystals filled by a fluid flow proposed in a previous paper, in the framework of rational extended irreversible thermodynamics with internal variables, is used to study the thermal, mechanical and transport properties of these materials. It is assumed that the medium under consideration has mass density constant, the body force and heat source distribution are negligible and the structural permeability tensor, its gradient, its flux, the heat flux and the fluid flow are independent variables besides the small strain tensor, the concentration of the fluid and its gradient, the temperature and its gradient. The constitutive equations

and the affinities are deduced, and the rate equations for dissipative fluxes and for the structural permeability tensor are worked out and it is seen that porous channels in nanocrystals influence mechanical and transport properties. In particular the generalized equations Maxwell-Vernotte-Cattaneo and Fick-Nannemaker are obtained. The obtained results have applications in nanotechnology and other fields of applied sciences.

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