

## HEAT EQUATION FOR POROUS NANOSTRUCTURES FILLED BY A FLUID FLOW

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**ABSTRACT.** In a previous paper, in the framework of extended irreversible thermodynamics with internal variables, a model for nanostructures with thin porous channels filled by a fluid flow was developed. The porous defects of porous channels inside the structure, described by a permeability structure tensor, may have a strong influence on the effective thermal conductivity, and their own dynamics may couple in relevant way to the heat flux dynamics. Here, in the linear case a generalized telegraph heat equation for thermal perturbations with finite velocity is derived in the anisotropic and isotropic case for the nanosystems taken into account. The thermal disturbances are so fast that their frequency becomes of the order of reciprocal of the relaxation time, given, for instance, by the collision time of heat carriers. Furthermore, the complete system of equations describing the behaviour of the media under consideration is worked out and discussed. The obtained results have applications in "defect engineering" and an important technological interest.

### 1. Introduction

In this paper, in the framework of extended irreversible thermodynamics (see Prigogine 1961; De Groot and Mazur 1962; Kluitenberg 1984; Kröner 1988; Muschik 1993; Jou *et al.* 2000; Muschik and Restuccia 2006; Lebon *et al.* 2008; Vàn *et al.* 2008; Jou *et al.* 2010; Jou and Restuccia 2011; Maugin 2015; Berezovski and Vàn 2017), we propose an analysis of heat transport in elastic systems with very thin porous channels, filled by a fluid flow, acting as defects on the thermal conductivity. In fact, the porous density has 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, the thermal conductivity diminishes and this decrease is very important in nanodevices. These defects are described by the internal variable  $r_{ij}$ , the structural permeability tensor à la Kubik (1986), its gradient  $r_{ij,k}$  and its flux  $\mathcal{V}_{ijk}$  (the porous channels can self propagate because of changed conditions and surrounding conditions that are favorable). The heat conductivity may depend on the porous defects of these materials, but, reciprocally, the heat flux may modify, in some occasions, the dynamics of the porous defects, in such a way that the problem of heat transport may be a strongly coupled in such systems. The topic of "defect engineering" is of relevant

interest nowadays in several technological sectors. In Scheidegger (1960), Bear *et al.* (1968), Dullien (1979), Wilmanski (2000), Restuccia (2005, 2010), Famà and Restuccia (2019), and Restuccia *et al.* (2020), models for porous media, with some applications, were developed. In Restuccia and Maruszewski (1991, 1995), Giambò *et al.* (2002), Restuccia (2005), Germanò and Restuccia (2007), Restuccia and Maruszewski (2008), Germanò and Restuccia (2010), Restuccia (2010), Jou and Restuccia (2018a,b), and Restuccia (2019) thermodynamic models for crystals with defects, described by internal variables, with special applications, were formulated. The obtained results in this paper can be applied to nanocrystals with porous defects filled by a fluid flow. The study of the heat equation in nanosystems with defects is an open problem because of two main reasons: their small size, which makes that the system exhibits large fluctuations in contrast to macroscopic systems, and the strong gradients caused by relatively small temperature differences, which make that the system may be far from local equilibrium. A relatively high temperature gradient could produce, for instance, a migration of defects inside the system. In Ván (2001), Grmela *et al.* (2011), Lebon *et al.* (2011), Ván *et al.* (2011), Ván and Fülöp (2012), Lebon (2014), Kovács and Ván (2015), Both *et al.* (2016), Ciancio and Restuccia (2016), Restuccia (2016), Ván (2016), Jou and Restuccia (2018c), Ciancio and Restuccia (2019), and Famà *et al.* (2019) heat conduction problems, with some applications, were studied in the frame of extended irreversible thermodynamics. Here, we study the behavior of nanosystems (see Jou and Restuccia 2011; Sellitto *et al.* 2016) where we have situations of high-frequency thermal waves. Inside the volume elements the field disturbances have finite speeds and describe fast phenomena, and 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. 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 ( $d \leq l$ , i.e. the Knudsen number  $\frac{l}{d}$  is such that  $\frac{l}{d} \geq 1$ ). Thus, both situations have a clear physical meaning and, nowadays, a technological interest. Then, in extended thermodynamics it is essential to incorporate the fluxes among the state variables. In Sections 2, 3, in the framework of extended irreversible thermodynamics with internal variables, a model is presented for elastic defective nanosystems (crystals with porous channels, carbon nanotubes in a solid matrix and so on) where the internal structure is described by a structural permeability tensor à la Kubik (see (Kubik 1986; Maruszewski 1991), and Appendix), its gradient and its flux, chosen as independent variables in the thermodynamic state vector besides the heat flux, the fluid flow, the small strain tensor, the concentration of the fluid and its gradient, the temperature and its gradient (see Restuccia 2005, 2010). Also the second law restrictions, obtained by Liu's theorem, are presented. In Section 4 the constitutive equations, the affinities and the rate equations for dissipative fluxes and for the structural permeability tensor, derived in a previous paper by Restuccia *et al.* (2020) in the anisotropic and linear case, are illustrated. In Section 5 a generalized telegraph heat equation with finite velocity for the thermal disturbances, is derived in the anisotropic and isotropic case. In Section 6 the closure of the system of equations describing the behaviour of the media under consideration is obtained and commented. This study has a technological interest in very miniaturized systems (nanotechnology), in high-frequency processes or in the production of new materials with sophisticated microstructures and particular thermal properties. The models of porous solids may have relevance in important

advances in the description of problems and phenomena that accompany flow of mass in porous structures and find applications in many fundamental sectors: geology, biology, medical sciences, technology of materials and other applied sciences.

## 2. A model for nanosystems with porous defects filled by a fluid flow in the framework of extended thermodynamics

In Sections 2 and 3 we present a model, developed in the framework of extended thermodynamics with internal variables (see Restuccia 2005, 2010; Restuccia *et al.* 2020) to study porous nanostructures filled by fluid flow. The fields acting inside them are: the mechanical field, described by the symmetric total stress tensor  $\tau_{ij}$ , related to the whole body considered as a mixture, and the small strain tensor  $\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$ , being  $\mathbf{u}$  the displacement field; the thermal field, described by the temperature  $T$ , its gradient  $T_{,i}$  and the heat flux  $q_i$ ; the fluid flow, described by three variables, the concentration of the fluid  $c$ , its gradient and the flux of this fluid  $j_i^c$ . The porous defects, disturbing the perfect periodicity of the crystal lattice, are modeled by the structural permeability tensor,  $r_{ij}$ , its gradient,  $r_{ij,k}$  and its flux,  $\mathcal{V}_{ijk}$ , describing the self-propagation of porous channels because of favorable and changed surrounding conditions. We use the standard Cartesian tensor notation in a rectangular coordinate system and refer the motion of our material system to a current configuration  $\mathcal{H}_t$ . Then, the state variables are represented by the set

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

where  $c_{,i}, T_{,i}$  and  $r_{ij,k}$  describe the nonlocal effects of the considered fields  $c, T, r_{ij}$ . We do not take into account the viscous effects, so that the field  $\frac{d\varepsilon_{ij}}{dt}$  (with  $\frac{d}{dt}$  the material time derivative) is not in the set  $C$ . We assume that mass of density  $\rho_1$  is the mass of the fluid transported through the elastic porous body of density  $\rho_2$ . Thus, the fluid and the elastic solid form a two-components mixture of density

$$\rho = \rho_1 + \rho_2, \quad (2)$$

where  $\rho_1 \ll \rho_2$ . We define the concentration  $c$  of the fluid as follows

$$c = \frac{\rho_1}{\rho}. \quad (3)$$

For the mixture of continua as a whole and also for each constituent, separately, the following continuity equations are satisfied

$$\dot{\rho} + \rho v_{i,i} = 0, \quad (4)$$

$$\frac{\partial \rho_1}{\partial t} + (\rho_1 v_{1i})_{,i} = 0, \quad (5)$$

$$\frac{\partial \rho_2}{\partial t} + (\rho_2 v_{2i})_{,i} = 0, \quad (6)$$

where we have supposed that there are not sources for the constituents  $\rho_1$  and  $\rho_2$ , a superimposed dot denotes the material derivative,  $v_i$  is the barycentric velocity of the whole medium,  $v_{1i}$  and  $v_{2i}$  are the velocities of the fluid particles and the particles of the elastic body, respectively, so that the barycentric velocity reads

$$\rho v_i = \rho_1 v_{1i} + \rho_2 v_{2i}. \quad (7)$$

The fluid flux is defined by

$$j_i^c = \rho_1(v_{1i} - v_i). \quad (8)$$

From Eq. (3) we obtain

$$\dot{c} = \frac{\dot{\rho}_1 \rho - \rho_1 \dot{\rho}}{\rho^2},$$

and using Eqs. (4), (5) and (8), we have

$$\begin{aligned} \rho \dot{c} &= \dot{\rho}_1 - \frac{\rho_1 \dot{\rho}}{\rho} = \dot{\rho}_1 + \rho_1 v_{i,i} \\ &= \frac{\partial \rho_1}{\partial t} + v_i \rho_{1,i} + \rho_1 v_{i,i} = -(\rho_1 v_{1i})_{,i} + v_i \rho_{1,i} + \rho_1 v_{i,i} \\ &= -[\rho_{1,i}(v_{1i} - v_i) + \rho_1(v_{1i,i} - v_{i,i})] = -j_{i,i}^c. \end{aligned} \quad (9)$$

The physical processes occurring inside the considered media are described by two groups of equations. The first set concerns the classical balance equations:

*the balance of mass* (obtained by (9))

$$\rho \dot{c} + j_{i,i}^c = 0; \quad (10)$$

*the momentum balance*

$$\rho \dot{v}_i - \tau_{ji,j} - f_i = 0, \quad (11)$$

where  $f_i$  denotes a body force;

*the internal energy balance*

$$\rho \dot{e} - \tau_{ji} v_{i,j} + q_{i,i} - \rho h = 0, \quad (12)$$

where  $h$  is the *heat source* and the gradient of the velocity of the body is given by

$$v_{i,j} = w_{ij} + \frac{d\varepsilon_{ij}}{dt}, \quad (13)$$

where  $w_{ij}$  is the antisymmetric part of  $v_{i,j}$ , defined by  $w_{ij} = \frac{1}{2}(v_{i,j} - v_{j,i})$ , and  $\frac{d\varepsilon_{ij}}{dt}$  is the symmetric part of  $v_{i,j}$ , defined by  $\frac{d\varepsilon_{ij}}{dt} = \frac{1}{2}(v_{i,j} + v_{j,i})$ .

In the sequel, for the sake of simplicity,  $h$  and  $f_i$  will be neglected. The second group of laws deals with the rate equations for the internal variable  $r_{ij}$  and for the fluxes  $j_i^c$ ,  $q_i$  and  $\mathcal{V}_{ijk}$

$${}^*r_{ij} + \mathcal{V}_{ijk,k} - \mathcal{R}_{ij}(C) = 0, \quad (14)$$

$$j_i^c - J_i^c(C) = 0, \quad (15)$$

$$q_i - Q_i(C) = 0, \quad (16)$$

$${}^*\mathcal{V}_{ijk} - V_{ijk}(C) = 0, \quad (17)$$

where the symbol (\*) denotes the Zaremba-Jaumann derivative defined for a vector, a second rank tensor and a general rank tensor as follows

$${}^*a_i = \dot{a}_i - w_{ik}a_k, \quad {}^*a_{ij} = \dot{a}_{ij} - w_{ik}a_{kj} - w_{jk}a_{ik}, \quad (18)$$

$${}^*a_{ij\dots m} = \dot{a}_{ij\dots m} - w_{ip}a_{pj\dots m} - w_{jp}a_{ip\dots m} - \dots - w_{mp}a_{ij\dots p}, \quad (19)$$

where  $\mathcal{R}_{ij}(C)$  is the source-like term which deals with the creation or annihilation of porous channels,  $J_i^c(C)$  is the fluid flow source,  $Q_i(C)$  is the heat source and  $V_{ijk}(C)$  is the source term for flux of the defects field. They are constitutive functions of the independent variables of the set (1). In (14)-(17) we use for  $w_{ij}$  the expression  $w_{ij} = v_{i,j} - \frac{\partial \varepsilon_{ij}}{\partial t}$ , in order to obtain relations in linear approximation.

In the rate equations (15)-(17) the flux terms of  $j_i^c$ ,  $q_i$  and  $\mathcal{V}_{ijk}$  are not considered in order to close the system of equations describing the media under consideration. The rate equations (14)-(17) are constructed obeying the objectivity and frame-indifference principles (see, for example, Muschik and Restuccia 2002; Hermann *et al.* 2004; Muschik and Restuccia 2008).

### 3. Second-law restrictions

To be sure that our considerations deal with real physical processes occurring in the considered body, all the admissible solutions of the proposed evolution equations should be restricted by the entropy inequality

$$\rho \dot{S} + \phi_{i,i} - \frac{\rho h}{T} \geq 0, \quad (20)$$

where  $S$  is the entropy density,  $\frac{\rho h}{T}$  is the external entropy production source and  $\phi_i$  is the entropy flux. In Restuccia 2005 the following and other results were derived, assuming that the density mass  $\rho$  of the considered defective nanocrystals is constant, applying Liu's theorem Liu 1972 (where all balance and rate equations of the problem are considered as mathematical constraints for the physical validity of the entropy inequality), and considering the set  $W$  of the constitutive functions,

$$W = \{ \tau_{ij}, e, \mathcal{R}_{ij}, J_i^c, Q_i, V_{ijk}, S, \phi_i, \Pi^c, \Pi_{ij}^r, \Pi_i^{j^c}, \Pi_i^q, \Pi_{ijk}^{\mathcal{V}} \},$$

(with  $\Pi^c$  the chemical potential of the fluid concentration field,  $\Pi_{ij}^r$  a potential related to the structural permeability field and  $\Pi_i^{j^c}$ ,  $\Pi_i^q$ ,  $\Pi_{ijk}^{\mathcal{V}}$  the generalized affinities conjugated to the respective fluxes  $j_i^c$ ,  $q_i$  and  $\mathcal{V}_{ijk}$ ):

*the state laws*, giving the partial derivatives of the free energy in terms of the respective conjugate thermodynamic variables

$$\tau_{ij} = \rho \frac{\partial F}{\partial \varepsilon_{ij}}, \quad S = -\frac{\partial F}{\partial T}, \quad \Pi^c = \frac{\partial F}{\partial c}, \quad \Pi_{ij}^r = \rho \frac{\partial F}{\partial r_{ij}}, \quad (21)$$

$$\frac{\partial F}{\partial c_{,i}} = 0, \quad \frac{\partial F}{\partial T_{,i}} = 0, \quad \frac{\partial F}{\partial r_{i,j,k}} = 0; \quad (22)$$

*the generalized affinities*

$$\Pi_i^{j^c} = \rho \frac{\partial F}{\partial j_i^c}, \quad \Pi_i^q = \rho \frac{\partial F}{\partial q_i}, \quad \Pi_{ijk}^{\mathcal{V}} = \rho \frac{\partial F}{\partial \mathcal{V}_{ijk}}; \quad (23)$$

*the residual inequality*, expressing the positive character of entropy production, and among other things, restricting the possible relations between the sources  $\mathcal{R}_{ij}(C)$ ,  $J_i^c(C)$ ,  $Q_i(C)$ ,

$V_{ijk}(C)$  and the generalized affinities  $\Pi_{ij}^r$ ,  $\Pi_i^c$ ,  $\Pi^q$ ,  $\Pi_{ijk}^v$

$$T \frac{\partial \phi_i}{\partial c} c_{,i} + T \frac{\partial \phi_i}{\partial T} T_{,i} + T \frac{\partial \phi_i}{\partial r_{jk}} r_{jk,i} - \Pi_{ij}^r \mathcal{R}_{ij} - \Pi_i^c J_i^c - \Pi_i^q Q_i - \Pi_{ijk}^v V_{ijk} \geq 0; \quad (24)$$

the entropy flux

$$\phi_k = \frac{1}{T} (q_k - \Pi^c J_k^c - \Pi_{ij}^r \mathcal{V}_{ijk}), \quad (25)$$

where the quantity  $-\frac{1}{T} (\Pi^c J_k^c + \Pi_{ij}^r \mathcal{V}_{ijk})$  is called extra entropy flux.

Furthermore, from equations (21)-(23) the free energy is a function of the following restricted set of independent variables

$$F = F(\varepsilon_{ij}, c, T, r_{ij}, J_i^c, q_i, \mathcal{V}_{ijk}). \quad (26)$$

#### 4. Constitutive relations, generalized affinities and rate equations

In Restuccia *et al.* 2020, expanding the free energy (26) up the second-order approximation around a thermodynamic equilibrium state, indicated by the subscript "0", introducing the deviations of the independent variables from this reference state, in particular

$$\theta = T - T_0, \quad \left| \frac{\theta}{T_0} \right| \ll 1, \quad \tilde{e} = e - e_0, \quad \left| \frac{\tilde{e}}{e_0} \right| \ll 1, \quad \mathcal{C} = c - c_0, \quad \left| \frac{\mathcal{C}}{c_0} \right| \ll 1,$$

$$\mathcal{S} = S - S_0, \quad \left| \frac{\mathcal{S}}{S_0} \right| \ll 1, \quad R_{ij} = r_{ij} - r_{0ij}, \quad \left| \frac{R_{ij}}{r_{0ij}} \right| \ll 1, \quad (27)$$

assuming

$$(\varepsilon_{ij})_0 = 0, \quad (\tau_{ij})_0 = 0, \quad (u_i)_0 = u_{0i}, \quad (v_i)_0 = v_{0i}, \quad (28)$$

and taking into account that

$$(J_i^c)_0 = 0, \quad (q_i)_0 = 0, \quad (\mathcal{V}_{ijk})_0 = 0, \quad (\Pi_{ij}^r)_0 = 0, \quad (\Pi^c)_0 = 0, \quad (\Pi_i^c)_0 = 0,$$

$$(\Pi_i^q)_0 = 0, \quad (\Pi_{ijk}^v)_0 = 0, \quad (29)$$

by virtue of equations (21)-(23), the following relations were obtained in the linear approximation:

the constitutive relations for the conjugate thermodynamic variables defined by (21) and (22)

$$\tau_{ij} = c_{ijlm} \varepsilon_{lm} - \lambda_{ij}^{\theta\varepsilon} \theta + \lambda_{ijlm}^{r\varepsilon} R_{lm} - \lambda_{ij}^{c\varepsilon} \mathcal{C}, \quad (30)$$

$$S = S_0 + \frac{\lambda_{ij}^{\theta\varepsilon}}{\rho} \varepsilon_{ij} + \frac{c_v}{T_0} \theta - \frac{\lambda_{ij}^{r\theta}}{\rho} R_{ij} - \frac{\lambda^{\theta c}}{\rho} \mathcal{C}, \quad (31)$$

$$\Pi_{ij}^r = \lambda_{ijlm}^{r\varepsilon} \varepsilon_{lm} + \lambda_{ij}^{r\theta} \theta + \lambda_{ijlm}^{rr} R_{lm} + \lambda_{ij}^{rc} \mathcal{C}, \quad (32)$$

$$\Pi^c = -\frac{\lambda_{ij}^{c\varepsilon}}{\rho} \varepsilon_{ij} + \frac{\lambda^{\theta c}}{\rho} \theta + \frac{\lambda_{ij}^{rc}}{\rho} R_{ij} + \frac{\lambda^c}{\rho} \mathcal{C}; \quad (33)$$

the generalized affinities

$$\Pi_{ijk}^v = \lambda_{ijklmn}^{vv} \mathcal{V}_{lmn} + \lambda_{ijkl}^{vq} q_l + \lambda_{ijk}^{vj^c} J_i^c, \quad (34)$$

$$\Pi_i^q = \lambda_{ijkl}^{qv} \mathcal{V}_{jkl} + \lambda_{ij}^{qq} q_j + \lambda_{ij}^{qj^c} J_j^c, \quad (35)$$

$$\Pi_i^{j^c} = \lambda_{ijkl}^{j^c v} \mathcal{V}_{jkl} + \lambda_{ij}^{j^c q} q_j + \lambda_{ij}^{j^c j^c} J_j^c. \quad (36)$$

In Eqs. (30)-(36)  $c_v$  denotes the specific heat,  $c_{ijlm}$  is the elastic tensor,  $\lambda_{ij}^{\theta\epsilon}$  are the thermoelastic constants and the other quantities express the simple and cross interactions among the fields present in the system. Moreover, the constant phenomenological coefficients satisfy the following symmetric relations, see Restuccia *et al.* (2020), because they are defined in terms of second derivatives of  $F$

$$\begin{aligned} c_{ijlm} &= c_{lmij} = c_{jilm} = c_{ijml} = c_{jiml} = c_{mlij} = c_{mlji} = c_{lmji}, \\ \lambda_{ijlm}^{r\epsilon} &= \lambda_{lmji}^{r\epsilon} = \lambda_{lmi j}^{r\epsilon} = \lambda_{jilm}^{r\epsilon} = \lambda_{ijml}^{r\epsilon} = \lambda_{jiml}^{r\epsilon} = \lambda_{mlji}^{r\epsilon} = \lambda_{mlij}^{r\epsilon}, \\ \lambda_{ijlm}^{rr} &= \lambda_{lmi j}^{rr} = \lambda_{ijml}^{rr} = \lambda_{jilm}^{rr} = \lambda_{jiml}^{rr} = \lambda_{mlji}^{rr} = \lambda_{mlij}^{rr} = \lambda_{mlji}^{rr}, \\ \lambda_{ij}^{\theta\epsilon} &= \lambda_{ji}^{\theta\epsilon}, \quad \lambda_{ij}^{qq} = \lambda_{ji}^{qq}, \quad \lambda_{ij}^{rc} = \lambda_{ji}^{rc}, \quad \lambda_{ij}^{c\epsilon} = \lambda_{ji}^{c\epsilon}, \quad \lambda_{ij}^{r\theta} = \lambda_{ji}^{r\theta}, \\ \lambda_{ijklmn}^{vv} &= \lambda_{lmnij k}^{vv}, \quad \lambda_{ijkl}^{vq} = \lambda_{lij k}^{vq}, \quad \lambda_{ij}^{j^c j^c} = \lambda_{ji}^{j^c j^c}, \quad \lambda_{ij}^{j^c q} = \lambda_{ji}^{j^c q}, \quad \lambda_{ij}^{vj^c} = \lambda_{ji}^{vj^c}. \end{aligned} \quad (37)$$

In Restuccia *et al.* 2020, in the case where we may use the material derivative instead of Zaremba-Jaumann derivative, the following rate equations were derived assuming that the source terms  $\mathcal{R}_{ij}$ ,  $V_{ijk}$ ,  $J_i^c$ ,  $Q_i$  have a form of linear polynomials with constant coefficients, in terms of the independent variables

$$\dot{r}_{ij} + \mathcal{V}_{ijk,k} = \beta_{ijkl}^1 \epsilon_{kl} + \beta_{ijkl}^2 r_{kl} + \beta_{ijk}^3 J_k^c + \beta_{ijk}^4 q_k + \beta_{ijklm}^5 \mathcal{V}_{klm} + \beta_{ijk}^6 c_{,k} + \beta_{ijk}^7 T_{,k} + \beta_{ijklm}^8 r_{kl,m}, \quad (38)$$

$$\dot{\mathcal{V}}_{ijk} = \gamma_{ijkl}^1 J_i^c + \gamma_{ijkl}^2 q_l + \gamma_{ijklmn}^3 \mathcal{V}_{lmn} + \gamma_{ijkl}^4 c_{,l} + \gamma_{ijkl}^5 T_{,l} + \gamma_{ijklmn}^6 r_{lm,n}, \quad (39)$$

$$\tau^q \dot{q}_i = \chi_{ij}^1 J_j^c - q_i + \chi_{ijkl}^3 \mathcal{V}_{jkl} + \chi_{ij}^4 c_{,j} - \chi_{ij}^5 T_{,j} + \chi_{ijkl}^6 r_{jk,l}, \quad (40)$$

where  $\chi_{ij}^1$  is the thermodiffusive kinetic tensor,  $\chi_{ij}^4$  the thermodiffusive tensor and  $\chi_{ij}^5$  the heat conductivity tensor,

$$\tau^{j^c} \dot{J}_i^c = -J_i^c + \xi_{ij}^2 q_j + \xi_{ijkl}^3 \mathcal{V}_{jkl} - \xi_{ij}^4 c_{,j} + \xi_{ij}^5 T_{,j} + \xi_{ijkl}^6 r_{jk,l}, \quad (41)$$

with  $\xi_{ik}^4$  and  $\xi_{ik}^5$  the diffusion tensor and the thermodiffusive tensor, respectively. The rate equation (40) generalizes Maxwell-Vernotte-Cattaneo relation

$$\tau^q \dot{q}_i = -q_i - \chi_{ij}^5 T_{,j},$$

that presents a relaxation time for the heat flux and describes thermal disturbances having finite velocity of propagation (see Cattaneo 1948 and Fichera 1992). The rate equation (41) for the mass flux generalizes the Fick-Nonnenmacher law

$$\tau^{j^c} \dot{J}_i^c = -J_i^c - \xi_{ij}^4 c_{,j},$$

that describes disturbances with finite velocity and presents a relaxation time for the fluid flux. Also the rate equations (38) and (39) allow finite speeds for the field disturbances and

describe fast phenomena whose relaxation times is comparable or higher than the relaxation times of the media under consideration, used in nanotechnology. In (38) - (41) the last three terms describe non-local effects, as they relate the rate equations to the inhomogeneities of the system.

## 5. Heat transport equation

In this Section we work out the temperature equation. Introducing the free energy given by  $F = e - TS$ , considering the material derivative of the free energy  $F$

$$\rho T \dot{S} = \rho \dot{e} - \rho S \dot{T} - \rho \dot{F}, \quad (42)$$

and taking into consideration the balance energy equation

$$\rho \dot{e} = \tau_{ij} \dot{\varepsilon}_{ij} - q_{i,i}, \quad (43)$$

(where the expression for the velocity gradient  $v_{i,j} = \dot{\varepsilon}_{ij} + \Omega_{ij}$  has been used), we obtain

$$\rho T \dot{S} = \tau_{ij} \dot{\varepsilon}_{ij} - q_{i,i} - \rho \dot{T} S - \rho \dot{F}. \quad (44)$$

From (44), calculating the material derivative of the free energy, we have

$$\begin{aligned} \rho T \dot{S} = & \tau_{ij} \dot{\varepsilon}_{ij} - q_{i,i} - \rho \dot{T} S - \rho \frac{\partial F}{\partial \varepsilon_{ij}} \dot{\varepsilon}_{ij} - \rho \frac{\partial F}{\partial T} \dot{T} - \rho \frac{\partial F}{\partial c} \dot{c} + \\ & - \rho \frac{\partial F}{\partial r_{ij}} \dot{r}_{ij} - \rho \frac{\partial F}{\partial \mathcal{V}_{ijk}} \dot{\mathcal{V}}_{ijk} - \rho \frac{\partial F}{\partial j_i^c} \dot{j}_i^c - \rho \frac{\partial F}{\partial q_i} \dot{q}_i. \end{aligned} \quad (45)$$

Finally, using the state laws (21), the definitions of the affinities (23), we have

$$\rho T \dot{S} = -q_{i,i} - \Pi_{ij}^r \dot{r}_{ij} - \Pi^c \dot{c} - \Pi_{ijk}^v \dot{\mathcal{V}}_{ijk} - \Pi_i^{jc} \dot{j}_i^c - \Pi_i^q \dot{q}_i. \quad (46)$$

Linearizing the equation (46) around the equilibrium state (27)-(29), we obtain

$$\rho (T_0 + \theta) (\dot{S}_0 + \dot{\mathcal{S}}) = -q_{i,i} - \Pi_{ij}^r [\dot{r}_{0ij} + \dot{R}_{ij}] - \Pi^c (\dot{c}_0 + \dot{\mathcal{C}}) - \Pi_{ijk}^v \dot{\mathcal{V}}_{ijk} - \Pi_i^{jc} \dot{j}_i^c - \Pi_i^q \dot{q}_i \quad (47)$$

and then,

$$\rho T_0 \dot{S} = -q_{i,i}. \quad (48)$$

Moreover, from equation (48), we have also

$$\tau^q \rho T_0 \ddot{S} = -\tau^q \dot{q}_{i,i}. \quad (49)$$

In (47) - (49), 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. From equations (31), (48), and (40), linearized around the considered reference equilibrium state, equation (49) takes the form

$$\begin{aligned} \tau^q \rho T_0 \left( \frac{\lambda_{ij}^{\theta\varepsilon}}{\rho} \dot{\varepsilon}_{ij} + \frac{c_v}{T_0} \dot{T} - \frac{\lambda_{ij}^{r\theta}}{\rho} \dot{r}_{ij} - \lambda^{\theta c} \dot{c} \right) = & -\rho T_0 \left( \frac{\lambda_{ij}^{\theta\varepsilon}}{\rho} \dot{\varepsilon}_{ij} + \frac{c_v}{T_0} \dot{T} - \frac{\lambda_{ij}^{r\theta}}{\rho} \dot{r}_{ij} - \lambda^{\theta c} \dot{c} \right) \\ & - \chi_{ij}^1 j_{j,i}^c - \chi_{ijkl}^3 \mathcal{V}_{jkl,i} - \chi_{ij}^4 c_{,ji} + \chi_{ij}^5 T_{,ji} - \chi_{ijkl}^6 r_{jk,li}. \end{aligned} \quad (50)$$



Finally, introducing

$$\gamma_{ij} = \frac{T_0}{\rho c_v} \lambda_{ij}^{\theta \varepsilon}, \quad \varphi = \frac{T_0}{c_v} \lambda^{\theta c}, \quad \eta_{ij} = \frac{T_0}{\rho c_v} \lambda_{ij}^{r \theta}, \quad (51)$$

$$v_{ij}^1 = \frac{\chi_{ij}^1}{\rho c_v}, \quad v_{ij}^4 = \frac{\chi_{ij}^4}{\rho c_v}, \quad k_{ij} = \frac{\chi_{ij}^5}{\rho c_v}, \quad (52)$$

and considering the case where we may replace the material derivative by the partial time derivative, we obtain a generalized telegraph equation, leading to finite speeds of propagation of thermal disturbances

$$\tau^q \ddot{T} + \dot{T} = k_{ij} T_{,ij} - \gamma_{ij} (\tau^q \ddot{\varepsilon}_{ij} + \dot{\varepsilon}_{ij}) + \varphi (\tau^q \ddot{c} + \dot{c}) + \eta_{ij} (\tau^q \ddot{r}_{ij} + \dot{r}_{ij}) - v_{ij}^1 j_{ij}^c - v_{ij}^4 c_{,ji}, \quad (53)$$

where the contributions of the fields  $\mathcal{V}_{jkl,i}$  and  $R_{jk,li}$  have been neglected.

In the case where the existence of spatial symmetry properties in the considered medium are such that it is *isotropic with respect to all rotations and to inversion of the frame of axes* (under orthogonal transformations) we have that the polar vectors  $L_i$  vanish, i.e.  $L_i = 0$ , the polar tensors of order two keep the form  $L_{ij} = L \delta_{ij}$ , the polar tensors of order three vanish, i.e.  $L_{ijk} = 0$ .

Then, we have

$$k_{ij} = k \delta_{ij}, \quad \gamma_{ij} = \gamma \delta_{ij}, \quad \eta_{ij} = \eta \delta_{ij}, \quad v_{ij}^1 = v^1 \delta_{ij}, \quad v_{ij}^4 = v^4 \delta_{ij}, \quad (54)$$

so that the heat equation (53) becomes

$$\tau^q \ddot{T} + \dot{T} = k T_{,ii} - \gamma (\tau^q \ddot{\varepsilon}_{ii} + \dot{\varepsilon}_{ii}) + \varphi (\tau^q \ddot{c} + \dot{c}) + \eta (\tau^q \ddot{r}_{ii} + \dot{r}_{ii}) - v^1 j_{i,i}^c - v^4 c_{,ii}, \quad (55)$$

leading to thermal disturbances with finite speed of propagation, which is so fast that its frequency becomes of the order of reciprocal of the internal relaxation time, given, for instance, by the collision time of the heat carriers (phonons). In the case of perfect nanostructures, without deformations, porous channels and fluid flow inside, Eq. (53) reduces to the telegraph equation

$$\tau^q \ddot{T} + \dot{T} = k T_{,ii}, \quad (56)$$

whose solution is well known.

From (56) it is seen that, when the thermal disturbances have infinite velocity, the parabolic Fourier heat equation is obtained

$$\dot{T} = k T_{,ii}, \quad (57)$$

describing the diffusion of these perturbations.

Also, from (56) we derive that if the contribution of the partial time derivative of the temperature field is negligible, the thermal perturbations obey the hyperbolic heat equation

$$\ddot{T} = \frac{k}{\tau^q} T_{,ii}, \quad (58)$$

that admits wave propagation.

In Restuccia *et al.* (2020), from (12), taking into account (27)<sub>2</sub>, using (48) and the time derivative (linearized) of relation (31), we obtain the following first law of Thermodynamics, where the second order term  $\tau_{ij} v_{i,j}$  has been neglected

$$\rho \dot{\varepsilon} + T_0 \lambda_{ij}^{\theta \varepsilon} \dot{\varepsilon}_{i,j} + \rho c_v \dot{T} - T_0 \lambda_{ij}^{r \theta} \dot{r}_{ij} - T_0 \lambda^{\theta c} \dot{c} = 0. \quad (59)$$

## 6. Closure of system of governing equations

In this Section, to close the system of equations describing linear anisotropic porous nanocrystals filled by fluid flow, we linearize the balance equations (10), (11), the constitutive equations (30) and (31) and the rate equations (38)-(41) around the equilibrium state (27)-(29). Taking into account the linearized temperature equation (53) and internal energy balance equation (59), the definitions  $\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i})$  and  $v_i = \dot{u}_i$ , indicating the deviations of the fields from the thermodynamic equilibrium state by the same symbols of the fields themselves, and considering the case where we may replace the material derivative by the partial time derivative, we obtain the following closed system of 45 equations for 45 unknowns: 1 for  $c$ , 3 for  $j_i^c$ , 3 for  $u_i$ , 6 for  $r_{ij}$ , 27 for  $\mathcal{V}_{ijk}$ , 1 for  $T$ , 1 for  $e$ , 3 for  $q_i$ ,

$$\rho \dot{c} + j_{i,i}^c = 0, \quad (60)$$

$$\rho \ddot{u}_i = c_{ijkl} u_{l,m,j} - \lambda_{ij}^{\theta e} T_{,j} + \lambda_{ijlm}^{r e} r_{lm,j} - \lambda_{ij}^{c e} c_{,j}, \quad (61)$$

$$\begin{aligned} \dot{r}_{ij} + \mathcal{V}_{ijk,k} = & \frac{1}{2} \beta_{ijkl}^1 (u_{k,l} + u_{l,k}) + \beta_{ijkl}^2 r_{kl} + \beta_{ijk}^3 j_k^c + \beta_{ijk}^4 q_k + \beta_{ijklm}^5 \mathcal{V}_{klm} \\ & + \beta_{ijk}^6 c_{,k} + \beta_{ijk}^7 T_{,k} + \beta_{ijklm}^8 r_{kl,m}, \end{aligned} \quad (62)$$

$$\dot{\mathcal{V}}_{ijk} = \gamma_{ijkl}^1 j_l^c + \gamma_{ijkl}^2 q_l + \gamma_{ijklmn}^3 \mathcal{V}_{lmn} + \gamma_{ijkl}^4 c_{,l} + \gamma_{ijkl}^5 T_{,l} + \gamma_{ijklmn}^6 r_{lm,n}, \quad (63)$$

$$\tau^q \dot{q}_i + q_i = \chi_{ij}^1 j_j^c + \chi_{ijkl}^3 \mathcal{V}_{jkl} + \chi_{ij}^4 c_{,j} - \chi_{ij}^5 T_{,j} + \chi_{ijkl}^6 r_{jk,l}, \quad (64)$$

$$\tau^j \dot{j}_i^c + j_i^c = \xi_{ij}^2 q_j + \xi_{ijkl}^3 \mathcal{V}_{jkl} - \xi_{ij}^4 c_{,j} + \xi_{ij}^5 T_{,j} + \xi_{ijkl}^6 r_{jk,l}, \quad (65)$$

$$\begin{aligned} \tau^q \dot{T} + \dot{T} = & k_{ij} T_{,ij} - \gamma_{ij} (\tau^q \dot{u}_{i,j} + \dot{u}_{i,j}) + \varphi (\tau^q \dot{c} + \dot{c}) + \eta_{ij} (\tau^q \dot{r}_{ij} + \dot{r}_{ij}) \\ & - v_{ij}^1 j_{j,i}^c - v_{ij}^4 c_{,ji}, \end{aligned} \quad (66)$$

$$\rho \dot{e} = -T_0 \lambda_{ij}^{\theta e} \dot{u}_{i,j} - \rho c_v \dot{T} + T_0 \lambda_{ij}^{r \theta} \dot{r}_{ij} + T_0 \lambda^{\theta c} \dot{c}. \quad (67)$$

In equations (61) and (67) the symmetry of  $c_{ijklm}$  and  $\lambda_{ij}^{\theta e}$  have been used (see (37)<sub>1</sub> and (37)<sub>4</sub>). In equation (66) the symmetry of  $\gamma_{ij}$  have been used (see (51)<sub>1</sub>). Also, the disturbances of the structural permeability field and its flux have finite velocity and present a relaxation time. Furthermore, also in the case where we do not take into consideration equation (67) for the internal energy, the system of equations (60) - (66) is still closed.

## 7. Conclusions

In this paper we have considered a nanosystem with defects of porous channel filled by fluid flow. We have presented a model in which the the porous defects are considered as an internal variable with its own dynamics. This allows a richer description of the system than simply assuming these defects as a static given parameter. The presence of these defects obviously has an influence on the thermal conductivity. In the linear case, the constitutive relations, the rate equations for the internal variables and the heat and fluid fluxes are presented, and in the anisotropic and isotropic case a generalized telegraph heat equation, with finite velocity for the thermal disturbances, is derived that may have applications in describing the thermal behaviour of the considered nanostructures, 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 the fluxes towards their respective local equilibrium value.

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### Appendix

**The structural permeability tensor à la Kubik.** Let us consider a representative elementary sphere volume  $\Omega$  of a structure with pores filled by fluid, large enough to provide a statistical representation of all the properties of this structure, where the porous channels resemble a network of infinitesimally thin tubes.  $\Omega = \Omega^s + \Omega^p$ , with  $\Omega^s$  and  $\Omega^p$  the solid space and the pore space of the elementary volume. Furthermore, we indicate by  $\Gamma$  the central sphere section given by  $\Gamma = \Gamma^s + \Gamma^p$ , with  $\Gamma^s$  and  $\Gamma^p$  the solid area and the pore area of the elementary volume. The orientation in  $\Gamma$  in  $\Omega$  is given by the normal vector  $\mu$ . All the microscopic quantities are described with respect to the  $\xi_i$  coordinates, while the macroscopic quantities are described with respect to the  $x_i$  coordinates ( $i = 1, 2, 3$ ). In Figure 1 we see the averaging scheme regarding a pore structure (see Kubik 1986; Maruszewski 1991). Since all pores are considered to be interconnected the effective volume porosity is

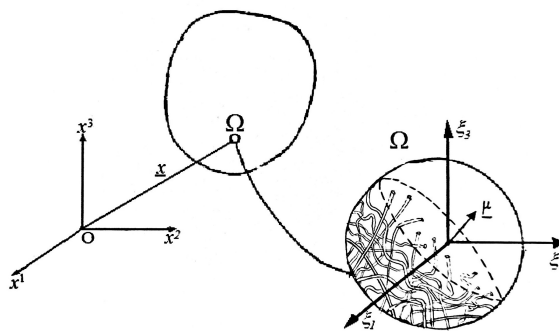


FIGURE 1. The averaging scheme.

completely defined as  $f_v = \frac{\Omega^p}{\Omega}$ , supposed constant, in such way that the present analysis is restricted to media which are homogeneous with respect to volume porosity.

Then, let  $\alpha(\xi)$  be any scalar, spatial vector or second order tensor, describing a microscopic property of the flux of some physical field, flowing through the channel porous space  $\Omega^p$ , with respect to the  $\xi$  coordinates. We assume that such quantity is zero in the solid space  $\Omega^s$  and on  $\Gamma^s$ . In such a medium we introduce a so called structural permeability tensor à la Kubik, responsible for the structure of a network of porous channels, for any property of a flux of some physical field  $\alpha(x)$  (in Kubik 1986 this tensor was introduced for

the velocity field  $\boldsymbol{v}$ ) in the following way

$$\bar{\alpha}_i(\boldsymbol{x}) = r_{ij}(\boldsymbol{x}) \hat{\alpha}_j(\boldsymbol{x}). \quad (68)$$

Eq. (68) gives a linear mapping between the bulk-volume average quantity  $\bar{\alpha}(\boldsymbol{x})$  and the porous area average of the same quantity passing through the pore area  $\Gamma^p$ , indicated by  $\hat{\alpha}(\boldsymbol{x})$ , given by

$$\bar{\alpha}(\boldsymbol{x}) = \frac{1}{\Omega} \int_{\tilde{\Omega}} \alpha(\boldsymbol{\xi}) d\tilde{\Omega}, \quad \boldsymbol{\xi} \in \Omega^p, \quad \hat{\alpha}(\boldsymbol{x}) = \frac{1}{\Gamma^p} \int_{\tilde{\Gamma}} \alpha(\boldsymbol{\xi}) d\tilde{\Gamma}, \quad \boldsymbol{\xi} \in \Gamma^p, \quad (69)$$

where the quantities  $\bar{\alpha}(\boldsymbol{x})$  and  $\hat{\alpha}(\boldsymbol{x})$  describe at macroscopic level the property of the flux of the physical quantity under consideration. The tensor  $r_{ij}$  is symmetric and describes the geometric structure of the porous media.

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