

A DERIVATION OF A GUYER-KRUMHANSL TYPE TEMPERATURE EQUATION IN CLASSICAL IRREVERSIBLE THERMODYNAMICS WITH INTERNAL VARIABLES

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ABSTRACT. In a previous paper, using the standard procedures of classical irreversible thermodynamics (CIT) with internal variables, we have shown that it is possible to describe thermal relaxation phenomena, obtaining some well-known results in extended irreversible thermodynamics (EIT). In particular, introducing two hidden variables, a vector and a second rank tensor, influencing the thermal transport phenomena in an undeformable medium, in the isotropic case, it was seen that the heat flux can be split in a first contribution $J^{(0)}$, governed by Fourier law, and a second contribution $J^{(1)}$, obeying Maxwell-Cattaneo-Vernotte equation (MCV), in which a relaxation time is present. In this contribution, using the obtained results, we work out a temperature equation, that in the one-dimensional case is a Guyer-Krumhansl type temperature equation, which contains as particular cases Maxwell-Cattaneo-Vernotte and Fourier temperature equations. Furthermore, in the case where n internal variables describe relaxation thermal phenomena, an analogous Guyer-Krumhansl type temperature equation is derived. The obtained results have applications in describing fast phenomena and high-frequency thermal waves in nanosystems.

1. Introduction

In this paper we use the procedures of *classical irreversible thermodynamics* (CIT) with internal variables, that were developed by Eckart (1940a,b,c, 1948), De Groot (1951), Prigogine (1961), and De Groot and Mazur (1984) and many others (Meixner and Reik 1959; Coleman and Gurtin 1967; Kluitenberg 1984; Maugin and Muschik 1994a,b).

The flexibility of the methodologies used in CIT with internal variables consists in the fact that “*a priori*” the physical meaning of these internal variables is not specified but only their influence on particular types of occurring phenomena in the considered medium is assumed. This feature has allowed scientists to be able to apply the CIT to a wide-scale phenomena in continuous media. In particular, relaxation phenomena were studied by the authors in rheological media (Kluitenberg and V. Ciancio 1978; V. Ciancio and Kluitenberg 1979; Kluitenberg 1984; V. Ciancio and Kluitenberg 1989) and in polarizable and magnetizable media (Restuccia and Kluitenberg 1987, 1988; V. Ciancio 1989; Restuccia and Kluitenberg 1989; V. Ciancio, Restuccia, and Kluitenberg 1990; Restuccia and Kluitenberg 1990;

Restuccia 2010, 2014) with theoretical results confirmed by some experimental data (A. Ciancio, V. Ciancio, and Farsaci 2007; V. Ciancio, Bartolotta, and Farsaci 2007; V. Ciancio, Farsaci, and Di Marco 2007; V. Ciancio, A. Ciancio, and Farsaci 2008; A. Ciancio 2011).

Parallel approaches were worked out in *rational extended thermodynamics* (RET) (Müller and Ruggeri 1998; Ruggeri and Sugiyama 2015) and in the frame of *extended irreversible thermodynamics* (EIT) (Jou, Casas-Vazquez, and Lebon 2010; Jou and Restuccia 2011), which, with considerations suggested by kinetic theory, consider an entropy depending on the fluxes beside the classical variables. In this paper, we use some results obtained in V. Ciancio and Restuccia (2016), where, considering an undeformable medium, using the systematic methodologies of CIT, we have shown that thermal relaxation phenomena may be studied with the aid of internal thermodynamic variables, obtaining some well-known equations in extended irreversible thermodynamics (EIT). In particular, in V. Ciancio and Restuccia (2016), introducing two internal variables, a vector and a second rank tensor, influencing the thermal transport phenomena, the phenomenological equations for these variables and the heat flux were derived. In the isotropic case, when the medium has symmetry properties that, under orthogonal transformations, are invariant with respect to all rotations and inversions of the frame of axes, it was obtained that the heat flux can be split in two parts: a first contribution obeying Fourier equation, describing thermal disturbances with infinite velocity, and a second one governed by a Maxwell-Cattaneo-Vernotte (MCV) equation, where a relaxation time is present, that allows a thermal propagation with finite speed (Maxwell 1872; Cattaneo 1948; Vernotte 1958; Gurtin and Pipkin 1968; Fichera 1992). Also, it was shown that the vectorial and the tensorial variables are connected with the heat flux and its gradient, respectively. In the framework of extended irreversible thermodynamics, Maxwell-Cattaneo-Vernotte equation was achieved incorporating the heat flux in the state variables and introducing some basic assumptions of simplicity (Jou, Casas-Vazquez, and Lebon 2010).

Here, first, using the results obtained in V. Ciancio and Restuccia (2016), we work out the temperature equation, that in the one-dimensional case is a Guyer-Krumhansl type equation (see Guyer and Krumhansl 1966a,b), which contains as particular cases Maxwell-Cattaneo-Vernotte and Fourier temperature equations. Furthermore, in the case where n internal variable describe relaxation thermal phenomena (see V. Ciancio and Verhás 1991) an analogous equation Guyer-Krumhansl type temperature equation is derived. In particular, in Sections 2, 3 and 4 a suitable non-equilibrium entropy for an undeformable material is assumed, depending on the internal energy and two internal variables influencing the thermal phenomena, the entropy production is analyzed, the phenomenological equations for an undeformable medium are presented and commented, and in the isotropic case the rate equation for the heat flux, split in a first contribution, obeying Fourier equation, and the second one satisfying MCV equation, is discussed. In Section 5, using these results, we derive a temperature equation, that in the one-dimensional case is of Guyer-Krumhansl type, which contains as particular cases Maxwell-Cattaneo-Vernotte and Fourier type temperature equations. In Sections 6 and 7 we treat the case where n vectorial internal variables describe relaxation thermal phenomena, and in the isotropic case where the heat flux is split in the sum of $n + 1$ contributions, the first one satisfying Fourier equation and the other ones n equations of MCV type, assuming that all the relaxation times for these last n contributions are equal, also a Guyer-Krumhansl type temperature equation is derived.

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 the fluxes towards their respective local-equilibrium value. In these nanosystems we have situations of high-frequency thermal waves (see Restuccia 2016).

2. Governing equations

In a previous paper a suitable non-equilibrium entropy for an undeformable material, depending on internal energy and two internal variables influencing the thermal phenomena, was assumed by the authors (V. Ciancio and Restuccia 2016). By the analysis of the entropy production, the phenomenological equations were derived. In particular, the thermodynamic state space is chosen as follows

$$C = C(u, \xi, \nabla \xi) \tag{1}$$

and the entropy function is assumed having the form

$$s(u, \xi, \nabla \xi) = s^{(eq)}(u) - \frac{1}{2} m_{\alpha\beta}^{(1)} \xi_\alpha \xi_\beta - \frac{1}{2} m_{\alpha\beta\gamma\delta}^{(2)} \Lambda_{\alpha\beta} \Lambda_{\gamma\delta}, \tag{2}$$

with

$$\Lambda_{\alpha\beta} \stackrel{\text{def}}{=} \left(\nabla \xi \right)_{\alpha\beta} \stackrel{\text{def}}{=} \frac{\partial \xi_\alpha}{\partial x^\beta}, \tag{3}$$

and

$$m_{\alpha\beta}^{(1)} = m_{\beta\alpha}^{(1)}, \quad m_{\alpha\beta\gamma\delta}^{(2)} = m_{\gamma\delta\alpha\beta}^{(2)} \quad (\alpha, \beta, \gamma, \delta = 1, 2, 3), \tag{4}$$

where $s^{eq}(u)$ is the equilibrium entropy function depending on the internal energy u , $m_{\alpha\beta}^{(1)}$ and $m_{\alpha\beta\mu\nu}^{(2)}$ are constitutive tensors characterizing the material coefficients and the usual summation convention for dummy indices is used. By virtue of (2) the following definitions are introduced

$$\left\{ \begin{array}{l} \frac{1}{T} = \frac{\partial s}{\partial u}, \\ \frac{\partial s}{\partial \xi_\alpha} = -m_{\alpha\beta}^{(1)} \xi_\beta \\ \frac{\partial s}{\partial \Lambda_{\alpha\beta}} = -m_{\alpha\beta\gamma\delta}^{(2)} \Lambda_{\gamma\delta}. \end{array} \right. \tag{5}$$

Using Eqs. (2) and (5) the so-called Gibbs relation is obtained

$$T ds = du - T m_{\alpha\beta}^{(1)} \xi_\alpha d\xi_\beta - T m_{\alpha\beta\gamma\delta}^{(2)} \Lambda_{\alpha\beta} d\Lambda_{\gamma\delta}. \tag{6}$$

From Eq. (6) the following expression is derived

$$\rho T \frac{ds}{dt} = \rho \frac{du}{dt} - \rho T m_{\alpha\beta}^{(1)} \xi_\alpha \frac{d\xi_\beta}{dt} - \rho T m_{\alpha\beta\gamma\delta}^{(2)} \Lambda_{\alpha\beta} \frac{d\Lambda_{\gamma\delta}}{dt}, \tag{7}$$

where d/dt is the material derivative defined as follows

$$\frac{d}{dt} = \frac{\partial}{\partial t} + v_\alpha \frac{\partial}{\partial x_\alpha} \tag{8}$$

and v_α is the velocity field.

The balance equation for the specific internal energy u is considered in the form

$$\rho \frac{du}{dt} + \nabla \cdot J^{(q)} = 0, \quad (9)$$

where $J^{(q)}$ is the heat flow.

With the aid of Eq. (9) the following entropy balance for the specific entropy s (*i.e.* the entropy per unit of mass) is obtained

$$\rho \frac{ds}{dt} = -\nabla \cdot \left(\frac{J^{(q)}}{T} \right) + \sigma^{(s)}, \quad (10)$$

where $J^{(eq)}/T$ is the entropy flow and $\sigma^{(s)}$ is the non-negative entropy production ($\sigma^{(s)} \geq 0$) per unit volume and per unit time, given by

$$\begin{aligned} \sigma^{(s)} = T^{-1} \left[-T^{-1} J^{(q)} \cdot \nabla T - \rho T m_{\alpha\beta}^{(1)} \xi_\alpha \frac{d\xi_\beta}{dt} + \right. \\ \left. - \rho T m_{\alpha\beta\gamma\delta}^{(2)} \Lambda_{\alpha\beta} \frac{d\Lambda_{\gamma\delta}}{dt} \right]. \end{aligned} \quad (11)$$

From Eq. (11) it is seen that the entropy production is additively composed of three contributions: the first term arising from heat conduction, the second and third terms connected with the entropy production due to the thermal relaxation, described by the internal variable and its gradient. Furthermore, in the entropy production (11) each term is the inner product of two factors: one is a flux and the other one is the thermodynamic force or “affinity” conjugate to the corresponding flux. $\sigma^{(s)}$ is zero if the system is in the thermodynamic equilibrium.

According to the usual procedure of non-equilibrium thermodynamics, for anisotropic media the following linear phenomenological equations are obtained

$$\begin{aligned} J_\alpha^{(q)} = L_{\alpha\beta}^{(q,q)} \left(-T^{-1} \frac{\partial T}{\partial x^\beta} \right) + L_{\alpha\beta}^{(q,1)} \left(-\rho T m_{\beta\mu}^{(1)} \frac{d\xi_\mu}{dt} \right) + \\ L_{\alpha\gamma\delta}^{(q,2)} \left(-\rho T m_{\mu\nu\gamma\delta}^{(2)} \Lambda_{\mu\nu} \right), \end{aligned} \quad (12)$$

$$\begin{aligned} \xi_\alpha = L_{\alpha\beta}^{(1,q)} \left(-T^{-1} \frac{\partial T}{\partial x^\beta} \right) + L_{\alpha\beta}^{(1,1)} \left(-\rho T m_{\beta\mu}^{(1)} \frac{d\xi_\mu}{dt} \right) + \\ L_{\alpha\gamma\delta}^{(1,2)} \left(-\rho T m_{\mu\nu\gamma\delta}^{(2)} \Lambda_{\mu\nu} \right), \end{aligned} \quad (13)$$

$$\begin{aligned} \frac{d}{dt} \Lambda_{\alpha\beta} = L_{\alpha\beta\mu}^{(2,q)} \left(-T^{-1} \frac{\partial T}{\partial x^\mu} \right) + L_{\alpha\beta\mu}^{(2,1)} \left(-\rho T m_{\mu\omega}^{(1)} \frac{d\xi_\omega}{dt} \right) + \\ L_{\alpha\beta\gamma\delta}^{(2,2)} \left(-\rho T m_{\mu\nu\gamma\delta}^{(2)} \Lambda_{\mu\nu} \right). \end{aligned} \quad (14)$$

Eq. (12) is a generalized Fourier law, where the phenomenological tensor $L_{\alpha\beta}^{(q,q)}$ is the thermal conductivity. Eqs. (13) and (14) describe the thermal relaxation of the internal macroscopic variables ξ and $\nabla\xi$.

The phenomenological coefficients $L_{\alpha\beta}^{(q,1)}$, $L_{\alpha\gamma\delta}^{(q,2)}$, $L_{\alpha\beta}^{(1,q)}$, $L_{\alpha\gamma\delta}^{(1,2)}$, $L_{\alpha\beta\mu}^{(2,q)}$ and $L_{\alpha\beta\mu}^{(2,1)}$ represent the possible cross effects among the irreversible phenomena occurring inside the considered medium.

Being the heat flow, $J^{(q)}$, the internal variable, ξ , and its gradient, $\nabla\xi$, odd functions of the microscopic particle velocities while the temperature gradient ∇T , the time derivatives of ξ and its gradient are even functions of these velocities, the following Onsager-Casimir reciprocity relations are obtained

$$L_{\alpha\beta}^{(q,q)} = L_{\beta\alpha}^{(q,q)}, L_{\alpha\beta}^{(q,1)} = L_{\beta\alpha}^{(q,1)}, L_{\alpha\beta}^{(1,q)} = L_{\beta\alpha}^{(1,q)}, L_{\alpha\beta}^{(1,1)} = L_{\beta\alpha}^{(1,1)}, \tag{15}$$

$$L_{\alpha\beta}^{(q,1)} = L_{\beta\alpha}^{(1,q)}, L_{\alpha\beta\gamma\delta}^{(2,2)} = L_{\gamma\delta\alpha\beta}^{(2,2)}, L_{\alpha\gamma\delta}^{(q,2)} = -L_{\gamma\delta\alpha}^{(2,q)}, L_{\alpha\gamma\delta}^{(1,2)} = -L_{\gamma\delta\alpha}^{(2,1)}. \tag{16}$$

By virtue of these relations, that reduce the number of independent components of the phenomenological tensors, substituting Eqs. (12)-(14) into (11), the entropy production assumes the form

$$\begin{aligned} T \sigma^{(s)} = & T^{-2} L_{\alpha\beta}^{(q,q)} \frac{\partial T}{\partial x^\alpha} \frac{\partial T}{\partial x^\beta} + 2\rho L_{\alpha\beta}^{(q,1)} m_{\beta\mu}^{(1)} \frac{\partial T}{\partial x^\alpha} \frac{d\xi_\mu}{dt} + \\ & (\rho T)^2 L_{\alpha\beta}^{(1,1)} m_{\beta\mu}^{(1)} m_{\alpha\omega}^{(1)} \frac{d\xi_\mu}{dt} \frac{d\xi_\omega}{dt} + \\ & (\rho T)^2 L_{\gamma\delta\omega\sigma}^{(2,2)} m_{\gamma\delta\alpha\beta}^{(2)} m_{\omega\sigma\mu\nu}^{(2)} \Lambda_{\alpha\beta} \Lambda_{\mu\nu} \geq 0. \end{aligned} \tag{17}$$

In this paper, from (17), we see that, being the entropy production a non-negative bilinear form in the components of temperature gradient, the components of the time derivative of the internal variable, the components of the internal variable gradient, many inequalities can be obtained for the components of the phenomenological tensors, resulting from the fact that all the elements of the main diagonal of the symbolic matrix associated to the bilinear form (63) must be non-negative, for instance

$$L_{\alpha\alpha}^{(q,q)} \geq 0, L_{\alpha\alpha}^{(1,1)} \geq 0, L_{\alpha\beta\beta\alpha}^{(2,2)} \geq 0, \quad (\alpha, \beta = 1, 2, 3) \tag{18}$$

and also all the major minors of this matrix must be non-negative, for example

$$L_{11}^{(q,q)} L_{22}^{(q,q)} - \left(L_{12}^{(q,q)} \right)^2 \geq 0. \tag{19}$$

V. Ciancio and Restuccia (2016) showed that when the considered media are isotropic (for which the symmetry properties are invariant under orthogonal transformations with respect to all rotations and to inversion of the frame of axes), the phenomenological tensors may assume the following form (see Jeffreys 1962),

$$L_{\alpha\beta}^{(q,q)} = T \lambda^{(q,q)} \delta_{\alpha\beta}, L_{\alpha\beta}^{(q,1)} = T^{-1} \mu^{(q)(1)} \delta_{\alpha\beta}, L_{\alpha\beta}^{(1,q)} = T \mu^{(1,q)} \delta_{\alpha\beta}, \tag{20}$$

$$L_{\alpha\beta}^{(1,1)} = T^{-1} \mu^{(1,1)} \delta_{\alpha\beta}, m_{\beta\mu}^{(1)} = a^{(1)} \delta_{\beta\mu}, \tag{21}$$

$$L_{\alpha\beta\gamma\delta}^{(2,2)} = \frac{1}{2} \eta_s^{(2,2)} (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) + \frac{1}{3} (\eta_v^{(2,2)} - \eta_s^{(2,2)}) \delta_{\alpha\beta} \delta_{\gamma\delta}, \tag{22}$$

$$m_{\mu\nu\gamma\delta}^{(2)} = T^{-1} \left[\frac{1}{2} b_s^{(2)} (\delta_{\mu\gamma} \delta_{\nu\delta} + \delta_{\mu\delta} \delta_{\nu\gamma}) + \frac{1}{3} (b_v^{(2)} - b_s^{(2)}) \delta_{\mu\nu} \delta_{\gamma\delta} \right]. \tag{23}$$

The tensors $L_{\alpha\beta\mu}^{(2,q)}$ and $L_{\alpha\beta\mu}^{(2,1)}$ are zero. Furthermore, from (16)₁, (20)₂ and (20)₃ it follows that

$$\mu^{(q,1)} = T^2 \mu^{(1,q)}. \tag{24}$$

Also, in the isotropic case, with the aid of the Onsager-Casimir reciprocity relations (15)-(16) and the positive definite character of the entropy production (17) the following inequalities for the phenomenological coefficients were derived

$$\lambda^{(q,q)} \geq 0, \quad \mu^{(1,1)} \geq 0. \quad (25)$$

Using (22) and (23), the phenomenological equation (14) became

$$\frac{d}{dt} \Lambda_{\alpha\beta} = -\rho b_s^{(2)} \eta_s^{(2,2)} \tilde{\Lambda}_{(\alpha\beta)} - \rho b_v^{(2)} \eta_v^{(2,2)} \Lambda \delta_{\alpha\beta}, \quad (26)$$

where

$$\Lambda_{(\alpha\beta)} = \frac{1}{2} (\Lambda_{\alpha\beta} + \Lambda_{\beta\alpha}), \quad \Lambda = \frac{1}{3} \Lambda_{(\alpha\beta)} \delta_{\alpha\beta}, \quad \tilde{\Lambda}_{(\alpha\beta)} = \Lambda_{(\alpha\beta)} - \Lambda \delta_{\alpha\beta}. \quad (27)$$

Observing that $\tilde{\Lambda}_{(\alpha\beta)} \delta_{\alpha\beta} = 0$ and $\Lambda = 3 \operatorname{div} \xi$, Eq. (26) gives:

$$\frac{d}{dt} \operatorname{div} \xi = -\rho b_v^{(2)} \eta_v^{(2,2)} \operatorname{div} \xi, \quad (28)$$

from which

$$\operatorname{div} \xi = (\operatorname{div} \xi)_0 \exp\left(-\rho b_v^{(2)} \eta_v^{(2,2)} t\right), \quad (29)$$

where

$$(\operatorname{div} \xi)_0 = (\operatorname{div} \xi)_{t=0} \quad (30)$$

and $b_v^{(2)} \eta_v^{(2,2)} \geq 0$.

Finally, by using (20) and (21), equations (12) and (13) read

$$\begin{cases} J_\alpha^{(q)} = -\lambda^{(q,q)} \frac{\partial T}{\partial x^\alpha} - \rho a^{(1)} \mu^{(q,1)} \frac{d\xi_\alpha}{dt} \\ \xi_\alpha = -\mu^{(1,q)} \frac{\partial T}{\partial x^\alpha} - \rho a^{(1)} \mu^{(1,1)} \frac{d\xi_\alpha}{dt}. \end{cases} \quad (31)$$

3. Heat transport equation

In this Section (see V. Ciancio and Restuccia 2016), we derive the rate equation for the heat flux J^q , expressed as sum of two contributions. In fact, in the case where $\rho a^{(1)} \mu^{(1,1)} \neq 0$, Eqs. (31) give

$$J^{(q)} = J^{(0)} + J^{(1)}, \quad (32)$$

where

$$J^{(1)} = \frac{\mu^{(q,1)}}{\mu^{(1,1)}} \xi, \quad (33)$$

$J^{(0)}$ satisfies a Fourier type equation

$$J^{(0)} = -\lambda^{(0)} \nabla T, \quad (34)$$

with $\lambda^{(0)}$ given by

$$\lambda^{(0)} = \lambda^{(q,q)} - T^2 \frac{(\mu^{(1,q)})^2}{\mu^{(1,1)}} \geq 0 \quad (35)$$

and the second contribution $J^{(1)}$, from (31)₂, obeys Maxwell-Cattaneo-Vernotte type, obtained in EIT introducing some basic assumptions of simplicity (Jou, Casas-Vazquez, and Lebon 2010),

$$\tau \frac{dJ^{(1)}}{dt} + J^{(1)} = -a \nabla T, \quad (36)$$

where τ is the relaxation time given by

$$\tau = \rho a^{(1)} \mu^{(1,1)} \quad \text{and} \quad a = T^2 \frac{(\mu^{(1,q)})^2}{\mu^{(1,1)}}, \quad (37)$$

with the assumption $a^{(1)} \geq 0$. Thus, from (33), $J^{(1)}$ is identified with the internal variable ξ , multiplied by a quantity linked to phenomenological constants.

4. Particular cases

From Eqs.(31)-(35) it was seen that if no cross-effects occur between the heat flux $J^{(q)}$ and the internal variable ξ , *i.e.* $\mu^{(q,1)} = 0$,

$$J^{(1)} = 0, \quad J^{(q)} = J^{(0)}$$

and for $J^{(q)}$ the well-known *Fourier law* is obtained, describing instantaneous thermal phenomena,

$$J^{(q)} = -\lambda^{(q,q)} \nabla T. \quad (38)$$

In the case where the cross-effects between the internal variable and the heat flux are present and the phenomenological coefficients satisfy the following condition

$$\lambda^{(q,q)} = T^2 \frac{(\mu^{(1,q)})^2}{\mu^{(1,1)}}, \quad (39)$$

$$J^{(0)} = 0, \quad J^{(q)} = J^{(1)}$$

and $J^{(q)}$ satisfies *Maxwell-Cattaneo-Vernotte equation*, describing thermal disturbances having finite propagation velocity and a relaxation time τ ,

$$\tau \frac{dJ^{(q)}}{dt} + J^{(q)} = -\lambda^{(q)(q)} \nabla T. \quad (40)$$

5. Guyer-Krumhansl type temperature equation

In this paper we derive a temperature equation, that, in the one-dimensional case, coincides with the Guyer-Krumhansl (GK) temperature equation. Guyer-Krumhansl model highlights the role of non-local effects in heat transport and is based on kinetic theory, taking into account special collision terms in the Boltzmann equation describing phono-lattice interactions (Guyer and Krumhansl 1966a,b).

By virtue of (32)-(33), the first law of thermodynamics (9) becomes

$$\rho \frac{du}{dt} + \nabla \cdot J^{(0)} + \nabla \cdot J^{(1)} = 0, \quad (41)$$

where $J^{(0)}$ and $J^{(1)}$ satisfy equations (34) and (36), with $\lambda^{(0)}$, τ and a given by (35) and (37), respectively. Assuming that the specific internal energy u is related to the temperature by

$$du = c_v dT, \quad (42)$$

being c_v the heat capacity per unit of mass at constant volume, and the considered undeformable medium is at rest, from (41) and (34) we have

$$\rho c_v \frac{\partial T}{\partial t} - \lambda^{(0)} \Delta T + \nabla \cdot J^{(1)} = 0, \quad (43)$$

and from (43) we obtain

$$\tau \rho c_v \frac{\partial^2 T}{\partial t^2} - \tau \lambda^{(0)} \frac{\partial}{\partial t} \Delta T + \tau \frac{\partial}{\partial t} (\nabla \cdot J^{(1)}) = 0. \quad (44)$$

Summing (43) and (44), by virtue of (36) we work out the following temperature equation

$$\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} - \alpha \Delta T - \eta \frac{\partial}{\partial t} (\Delta T) = 0, \quad (45)$$

where

$$\left\{ \begin{array}{l} \alpha = \frac{\lambda^{(0)} + a}{\rho c_v} = \frac{\lambda^{(q,q)}}{\rho c_v} \\ \eta = \frac{\tau \lambda^{(0)}}{\rho c_v}. \end{array} \right. \quad (46)$$

Equation (46) in the one-dimensional case is a Guyer-Krumhansl type temperature equation.

5.1. Maxwell-Cattaneo-Vernotte and Fourier temperature equations. In the case where the cross-effects between the internal variable and the heat flux are present and the phenomenological coefficients satisfy the following condition

$$\lambda^{(q,q)} \mu^{(1,1)} = T^2 (\mu^{(1,q)})^2, \quad (47)$$

by virtue of (34), (35) and (37)₂, from (46), one has

$$\lambda^{(0)} = 0, \quad a = \lambda^{(q,q)}$$

and (45) becomes:

$$\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} - \chi \Delta T = 0, \quad (48)$$

where

$$\chi = \frac{\lambda^{(q,q)}}{\rho c_v} \quad (49)$$

designates the thermal diffusivity. Eq. (48) is Maxwell-Cattaneo-Vernotte temperature equation of telegrapher type, describing thermal disturbances propagation with finite velocity, of technological interest in very miniaturized systems (nanotechnology), in high-frequency processes.

If in the medium the cross effects between the heat flux and the internal variable do not occur, from (24), (31) and (33) one has

$$\mu^{(q,1)} = \mu^{(1,q)} = 0 \quad \text{and} \quad J^{(1)} = 0, \quad (50)$$

This means that the heat flux (32), using (34) and (35), satisfies Fourier law, *i.e.*

$$J^{(q)} = J^{(0)} = -\lambda^{(0)} \nabla T, \tag{51}$$

and from (41) one obtains

$$\frac{\partial T}{\partial t} - \chi \Delta T = 0, \tag{52}$$

where

$$\chi = \frac{\lambda^{(q,q)}}{\rho c_v}. \tag{53}$$

Equation (52) is the classic Fourier heat diffusion equation. It is a parabolic differential equation leading to the paradox of thermal disturbances propagation with infinite speed.

6. Case of n internal variables

In this section, it is assumed that n microscopic phenomena occur in the considered undeformable medium, which give rise to thermal relaxation and that it is possible to describe the contributions of these phenomena introducing n vectorial internal variables, $\xi^{(i)}$ ($i = 1, 2, \dots, n$), in the expression for the entropy (see V. Ciancio and Verhás 1991)

$$s = s(u, \xi^{(1)}, \xi^{(2)}, \dots, \xi^{(n)}). \tag{54}$$

It is assumed that the entropy density has the form

$$s = s^{(eq)}(u) - \frac{1}{2} \sum_{k=1}^n (\xi^{(k)})^2, \tag{55}$$

where $s^{(eq)}(u)$ is the equilibrium entropy function. Using the following definitions

$$\frac{1}{T} \stackrel{\text{def}}{=} \frac{\partial s}{\partial u}, \tag{56}$$

$$\frac{\partial s}{\partial \xi_\alpha^{(k)}} = -\xi_\alpha^{(k)} \quad (k = 1, 2, \dots, n), \quad (\alpha = 1, 2, 3), \tag{57}$$

Gibbs relation is obtained in the form

$$T ds = du - T \sum_{k=1}^n \xi^{(k)} \cdot d\xi^{(k)}. \tag{58}$$

From (58) and the first law of thermodynamics (9), the entropy balance is given by (10), with

$$\sigma^{(s)} = T^{-1} \left[-T^{-1} J^{(q)} \cdot \nabla T - \rho T \sum_{k=1}^n \xi^{(k)} \cdot \frac{d\xi^{(k)}}{dt} \right]. \tag{59}$$

From (59) it is seen that the entropy production is additively composed by the sum of $n + 1$ contributions: the first one is due to heat conduction phenomena and the other n terms are due to the thermal relaxations of the internal variables. In (59) each term is a inner product of a flux and the affinity conjugate to it. According to the usual procedure of

non-equilibrium thermodynamics, by virtue of the form (59) for the entropy production, the following phenomenological equations for anisotropic media are obtained

$$J_{\alpha}^{(q)} = -T^{-1}L_{\alpha\beta}^{(q)(q)} \frac{\partial T}{\partial x^{\beta}} - \rho T \sum_{k=1}^n L_{\alpha\beta}^{(q)(k)} \frac{d\xi_{\beta}^{(k)}}{dt}, \tag{60}$$

$$\xi_{\alpha}^{(i)} = -T^{-1}L_{\alpha\beta}^{(i)(q)} \frac{\partial T}{\partial x^{\beta}} - \rho T \sum_{k=1}^n L_{\alpha\beta}^{(i)(k)} \frac{d\xi_{\beta}^{(k)}}{dt} \quad (i = 1, 2, \dots, n). \tag{61}$$

Equation (60) may be regarded as a generalization of Fourier law. The phenomenological tensor $L_{\alpha\beta}^{(q)(q)}$ is the thermal conductivity tensor. Equations (61) concern the thermal relaxation of n internal macroscopic variables $\xi^{(k)}$ ($k = 1, 2, \dots, n$).

The phenomenological tensors $L_{\alpha\beta}^{(q)(k)}$, $L_{\alpha\beta}^{(i)(q)}$, $L_{\alpha\beta}^{(i)(k)}$ ($k = 1, 2, \dots, n$) represent the possible cross effects among the irreversible phenomena. Since the heat flow $J^{(q)}$ and the internal variables $\xi^{(k)}$ are odd functions of the microscopic particle velocities, and the temperature gradient ∇T , the time derivatives of the internal variables $\frac{d\xi^{(k)}}{dt}$ are even functions of these velocities, Onsager-Casimir relations read

$$\begin{aligned} L_{\alpha\beta}^{(q)(q)} &= L_{\beta\alpha}^{(q)(q)}, & L_{\alpha\beta}^{(q)(k)} &= L_{\beta\alpha}^{(q)(k)}, & L_{\alpha\beta}^{(q)(k)} &= L_{\beta\alpha}^{(k)(q)}, \\ L_{\alpha\beta}^{(i)(q)} &= L_{\beta\alpha}^{(i)(q)}, & L_{\alpha\beta}^{(i)(k)} &= L_{\beta\alpha}^{(i)(k)} \quad (i, k = 1, 2, \dots, n). \end{aligned} \tag{62}$$

By virtue of these relations, that reduce the number of independent components of the phenomenological tensors, substituting equations (60), (61) into (59), the entropy production assumes the form

$$\begin{aligned} T \sigma^{(s)} &= T^{-2}L_{\alpha\beta}^{(q)(q)} \frac{\partial T}{\partial x^{\alpha}} \frac{\partial T}{\partial x^{\beta}} + 2\rho \sum_{i=1}^n L_{\alpha\beta}^{(q)(i)} \frac{\partial T}{\partial x^{\alpha}} \frac{d\xi_{\beta}^{(i)}}{dt} + \\ &(\rho T)^2 \sum_{i,k=1}^n L_{\alpha\beta}^{(i)(k)} \frac{d\xi_{\alpha}^{(i)}}{dt} \frac{d\xi_{\beta}^{(k)}}{dt} \geq 0. \end{aligned} \tag{63}$$

In this paper, we see from (63) that, being the entropy production a non-negative bilinear form in the components of temperature gradient and of the components of the time derivatives of the internal variables, many inequalities can be obtained for the components of the phenomenological tensors, for instance

$$L_{\alpha\alpha}^{(q)(q)} \geq 0, \quad L_{\alpha\alpha}^{(i)(k)} \geq 0, \quad (\alpha, \beta = 1, 2, 3), \quad (i, k = 1, 2, \dots, n) \tag{64}$$

and also

$$L_{11}^{(q)(q)}L_{22}^{(q)(q)} - \left(L_{12}^{(q)(q)}\right)^2 \geq 0. \tag{65}$$

In the case where the considered media are isotropic with respect to all rotations and inversion of the frame of axes, the phenomenological tensors may have the form

$$\begin{aligned} L_{\alpha\beta}^{(q)(q)} &= T\lambda^{(q)(q)}\delta_{\alpha\beta}, & L_{\alpha\beta}^{(q)(k)} &= T^{-1}\mu^{(q)(k)}\delta_{\alpha\beta}, \\ L_{\alpha\beta}^{(k)(q)} &= T^{-1}\mu^{(k)(q)}\delta_{\alpha\beta}, & L_{\alpha\beta}^{(i)(k)} &= T^{-1}\alpha^{(i)(k)}\delta_{\alpha\beta} \quad (i, k = 1, 2, \dots, n). \end{aligned} \tag{66}$$

Using relations (62) and (66), the phenomenological equations (60) and (61) become

$$J_{\alpha}^{(q)} = -\lambda^{(q)(q)} \frac{\partial T}{\partial x^{\alpha}} - \rho \sum_{k=1}^n \mu^{(q)(k)} \frac{d\xi^{(k)}}{dt},$$

$$\xi^{(i)} = -\mu^{(i)(q)} \frac{\partial T}{\partial x^{\alpha}} - \rho \alpha^{(i)} \frac{d\xi^{(i)}}{dt} \tag{67}$$

($i = 1, 2, \dots, n$),

where the diagonal form $\alpha^{(i)}$ of the matrix of the coefficients $\alpha^{(i)(k)}$ is chosen. Being $\alpha^{(i)} \geq 0$, see (64)₂ and (66)₄, from (67) one obtains (see V. Ciancio and Restuccia (2016))

$$J^{(q)} = \tilde{J}^{(0)} + \sum_{k=1}^n J^{(k)}, \tag{68}$$

where

$$J^{(k)} = \frac{\mu^{(q)(k)}}{\alpha^{(k)}} \xi^{(k)}, \tag{69}$$

and $\tilde{J}^{(0)}$ satisfies Fourier law

$$\tilde{J}^{(0)} = -\tilde{\lambda}^{(0)} \nabla T, \tag{70}$$

with

$$\tilde{\lambda}^{(0)} = \lambda^{(q)(q)} - \sum_{k=1}^n \lambda^{(k)}, \tag{71}$$

$$\lambda^{(k)} = T^2 \frac{(\mu^{(k)(q)})^2}{\alpha^{(k)}}, \tag{72}$$

and the n contributions $J^{(k)}$ obey n Maxwell-Cattaneo-Vernotte type equations

$$J^{(k)} + \tau^{(k)} \frac{dJ^{(k)}}{dt} = -\lambda^{(k)} \nabla T \quad (k = 1, 2, \dots, n), \tag{73}$$

where

$$\tau^{(k)} = \rho \alpha^{(k)} \quad (k = 1, 2, \dots, n). \tag{74}$$

Thus, from (69) the flux $J^{(k)}$ is identified with the internal variable $\xi^{(k)}$ multiplied by a quantity linked to phenomenological constants. We interpret these results in the light of the study achieved in this paper regarding the repercussion of the introduction of internal variables, that illustrate thermal relaxation phenomena. In the case where we introduce in the expression of the entropy n internal variables, describing n mesoscopic phenomena (electromagnetic radiation, acoustic waves, electron waves,...) inside the material, influencing the heat propagation, $J^{(q)}$ is split in $n + 1$ contributions: the first one $\tilde{J}^{(0)}$ governed by Fourier law, and the other ones $n J^{(k)}$ ($k = 1, 2, \dots, n$) obeying n Vernotte-Cattaneo type equations, with $\tau^{(k)}$ the corresponding thermal relaxation times, describing, in the frame of extended irreversible thermodynamics, relaxation thermal phenomena.

7. Guyer-Krumhansl type temperature equation in the case of n internal variables

Let us consider Eq.s (68)-(74). The first law of thermodynamics (9) takes the form

$$\rho \frac{du}{dt} + \nabla \cdot \tilde{J}^{(0)} + \sum_{k=1}^n \nabla \cdot J^{(k)} = 0. \quad (75)$$

Assuming that the specific internal energy u is related to the temperature by relation (42) $du = c_v dT$ and the considered undeformable medium is at rest, from (75) and (70) we have

$$\rho c_v \frac{\partial T}{\partial t} + \tilde{\lambda}^{(0)} \Delta T + \sum_{k=1}^n \nabla \cdot J^{(k)} = 0, \quad (76)$$

and assuming that all $\tau^{(k)}$ are equal, $\tau^{(k)} = \tau$, we have

$$\tau \rho c_v \frac{\partial^2 T}{\partial t^2} + \tau \tilde{\lambda}^{(0)} \frac{\partial}{\partial t} \Delta T + \tau \sum_{k=1}^n \frac{\partial}{\partial t} (\nabla \cdot J^{(k)}) = 0. \quad (77)$$

Summing (76) and (77), by virtue of (73), we work out the following temperature equation

$$\tau \rho c_v \frac{\partial^2 T}{\partial t^2} + \rho c_v \frac{\partial T}{\partial t} = \left(\tilde{\lambda}^{(0)} + \sum_{k=1}^n \lambda^{(k)} \right) \Delta T + \tau \tilde{\lambda}^{(0)} \frac{\partial}{\partial t} \Delta T, \quad (78)$$

that may be written in the following form

$$\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} - \alpha' \Delta T - \eta' \frac{\partial}{\partial t} (\Delta T) = 0, \quad (79)$$

with

$$\begin{cases} \alpha' = \frac{\tilde{\lambda}^{(0)} + \sum_{k=1}^n \lambda^{(k)}}{\rho c_v}, \\ \eta' = \frac{\tau \tilde{\lambda}^{(0)}}{\rho c_v}, \end{cases} \quad (80)$$

that represents in the one-dimensional case a Guyer-Krumhansl type temperature equation.

7.1. Fourier case. In the case where inside the considered medium there are not present cross effects among the irreversible phenomena from (68)-(72) one has

$$\mu^{(q)(k)} = \mu^{(k)(q)} = 0, \quad J^{(k)} = 0 \quad (k = 1, 2, \dots, n) \quad (81)$$

and for $J^{(q)}$, from Eq. (32), Fourier law is obtained

$$J^{(q)} = \tilde{J}^{(0)} = -\tilde{\lambda}^{(0)} \nabla T = -\lambda^{(q)(q)} \nabla T. \quad (82)$$

In this case, from (76) one has:

$$\frac{\partial T}{\partial t} - k \Delta T = 0, \quad (83)$$

with

$$k = \frac{\lambda^{(q)(q)}}{\rho c_v}, \quad (84)$$

that is the classic Fourier temperature equation.

7.2. Maxwell-Cattaneo-Vernotte case. In the case where the cross-effects among the heat flux and the internal variables are present and the phenomenological coefficients satisfy the following condition

$$\lambda^{(q)(q)} = \sum_{k=1}^n \frac{T^2(\mu^{(k)(q)})^2}{\alpha^{(k)}},$$

by virtue of (68)-(72), one has

$$\tilde{\lambda}^{(0)} = 0, \tag{85}$$

$$\tilde{J}^{(0)} = 0, \quad J^{(q)} = \sum_{k=1}^n J^{(k)},$$

and (79) becomes:

$$\tau \frac{\partial^2 T}{\partial t^2} + \frac{\partial T}{\partial t} - k \Delta T = 0, \tag{86}$$

where

$$k = \frac{\sum_{k=1}^n \lambda^{(k)}}{\rho c_v} = \frac{\lambda^{(q)(q)}}{\rho c_v} \tag{87}$$

is the thermal diffusivity. Eq. (86) is Maxwell-Cattaneo-Vernotte temperature equation of telegrapher type. Maxwell-Cattaneo-Vernotte model describes the heat transport with a finite velocity, with the presence of a relaxation time, but for example is insufficient to illustrate the second sound signals amplification and the ballistic phonon propagation phenomenon (Jou, Casas-Vazquez, and Lebon 2010).

8. Conclusions

In a previous paper, see V. Ciancio and Restuccia (2016), introducing in the entropy two internal variables, influencing thermal phenomena, without basic assumptions of simplicity and applying the methods of irreversible thermodynamics with internal variables, the phenomenological equations were derived in the anisotropic and isotropic cases for these variables. In the isotropic case, it was seen that the heat flux is split in two contributions: a first contribution $J^{(0)}$, governed by Fourier law, and a second contribution $J^{(1)}$, obeying Maxwell-Cattaneo-Vernotte equation, in which a relaxation time is present. In the framework of extended irreversible thermodynamics, Maxwell-Cattaneo-Vernotte equation was achieved incorporating the heat flux in the state variables and introducing some basic assumptions (Jou, Casas-Vazquez, and Lebon 2010).

In this paper, we have commented these previously obtained results, and we have studied thermal relaxation phenomena, working out a temperature equation, that in the one-dimensional case is a Guyer-Krumhansl type temperature equation, and contains as particular cases Maxwell-Cattaneo-Vernotte temperature equation of telegrapher type, admitting thermal propagation with finite velocity and Fourier temperature equation, leading to the paradox of thermal disturbances propagation with infinite speed. Also, in this paper we have treated the case where in an undeformable medium, the relaxation thermal phenomena are described by n vectorial hidden variables (see V. Ciancio and Verhás 1991) and it was shown that, in the isotropic case, the heat flux is split in the sum of $n + 1$ contributions, the first one obeying Fourier type equation and the other n obeying equations of Maxwell-Cattaneo-Vernotte type, each one having different relaxation time τ_k ($k = 1, 2, \dots, n$). Assuming that

all the relaxation times τ_k for these last n contributions are equal, also the temperature equation has been derived, that in the one-dimensional case is a Guyer-Krumhansl type temperature equation, containing Fourier and Maxwell-Cattaneo-Vernotte special cases. GK equation is based on kinetic theory and takes into consideration special collision terms in the Boltzmann equation describing phono-lattice interactions. The results worked out in this paper may have applications in describing the thermal behavior in nanosystems, where a 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. These situations have a clear physical meaning and, nowadays, a technological interest.

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