
BOLLETTINO UNIONE MATEMATICA ITALIANA

M. S. MONGIOVÌ, R. A. PERUZZA

Entropy flux far from equilibrium in solids and in non viscous gases

*Bollettino dell'Unione Matematica Italiana, Serie 8, Vol. 7-B (2004),
n.2, p. 381–396.*

Unione Matematica Italiana

http://www.bdim.eu/item?id=BUMI_2004_8_7B_2_381_0

L'utilizzo e la stampa di questo documento digitale è consentito liberamente per motivi di ricerca e studio. Non è consentito l'utilizzo dello stesso per motivi commerciali. Tutte le copie di questo documento devono riportare questo avvertimento.

*Articolo digitalizzato nel quadro del programma
bdim (Biblioteca Digitale Italiana di Matematica)
SIMAI & UMI*

<http://www.bdim.eu/>

Entropy Flux far From Equilibrium in Solids and in Non Viscous Gases.

M. S. MONGIOVÌ - R. A. PERUZZA (*)

Sunto. – *Una delle principali questioni che sorge nella termodinamica estesa riguarda il significato fisico della temperatura lontano dall'equilibrio. Alcuni autori definiscono temperatura termodinamica T_{th} il reciproco del coefficiente che lega il flusso di entropia e il flusso di calore. Altri autori, invece, definiscono temperatura di non-equilibrio θ il reciproco della derivata parziale dell'entropia rispetto all'energia a densità e flusso di calore costanti. Lo scopo fondamentale di questo lavoro è di determinare le espressioni complete del flusso di entropia in alcuni materiali quando vengono considerati fenomeni lontano dall'equilibrio termodinamico. Per tale scopo si utilizza la formulazione della termodinamica estesa, conosciuta come Termodinamica Estesa Razionale, che usa i moltiplicatori di Lagrange. Si prendono in esame due situazioni fisiche particolarmente semplici ma molto importanti: il caso della propagazione termica che avviene nei cristalli a bassa temperatura e il caso dei gas non viscosi soggetti a riscaldamento. Si mostra che la temperatura di non-equilibrio e la temperatura termodinamica in generale non coincidono, e si determinano le espressioni approssimate della loro differenza.*

Summary. – *One of the main question arising in Extended Thermodynamics concerns the physical meaning of the temperature far from equilibrium. Some authors define thermodynamic temperature T_{th} the inverse of the coefficient linking the entropy flux with the heat flux. Other authors, instead, define non-equilibrium temperature θ the inverse of the partial derivative of entropy with respect to energy, at density and heat flux constant. The aim of this paper is to determine the expression of entropy flux in some materials when phenomena far from equilibrium are considered, using the formulation of Extended Thermodynamics which uses the Lagrange multipliers, known as Rational Extended Thermodynamics. The case of thermal propagation that occurs in low-temperature crystals and the case of non viscous gases subject to heating are considered. It is shown that the non-equilibrium temperature and the thermodynamic temperature not agree, except near equilibrium, when second order terms in q_i can be neglected. Approximate expressions for T_{th} and θ are determined in both cases.*

(*) This work is supported by MIUR under grant *Nonlinear Mathematical Problems of Wave Propagation and Stability in Models of Continuous Media.*

1. – Introduction.

During the last decades a new thermodynamic formalism, known as Extended Thermodynamics (E.T.) [10, 20] has been developed, in order to describe rapid phenomena or materials in which the relaxation times of some fluxes are long. This theory, in fact, uses dissipative fluxes, beside traditional variables, as independent fields. When this new formalism is adopted and the entropy is considered to depend for example also on heat flux, it has been found that the entropy flux is also modified and new terms naturally appear.

In classical thermodynamics of solids or fluids, the absolute temperature (or the equilibrium temperature) is equal to the inverse of the coefficient linking entropy flux and heat flux and it is identical to the inverse of the partial derivative of entropy with respect to energy, at density constant. As known, if we consider a thermometer immersed in a system in which there is a heat flux, assuming that the wall between the thermometer and the system is ideal (i.e. in this wall no entropy is produced), from energy and entropy balance laws it can deduce that both entropy flux and heat flux are continuous across an ideal wall; for this reason, some authors [2, 3] define *thermodynamic temperature* T_{th} the inverse of the coefficient linking entropy flux with heat flux. Other authors [10, 11, 12], instead, define *non-equilibrium temperature* θ the inverse of the partial derivative of entropy with respect to energy, at density and heat flux constant [5].

The aim of this paper is to determine the expressions of the entropy flux in some materials when phenomena far from equilibrium are considered, using the formulation of E.T. which uses the Lagrange multipliers [14], known as Rational Extended Thermodynamics [20]. The case of thermal propagation that occurs in low-temperature crystals and the case of non viscous gases subject to heating, which are two simple but very important and representative physical situations, will be considered. It is shown that the non-equilibrium temperature and the thermodynamic temperature not agree, except near equilibrium, when second order terms in heat flux q_i can be neglected. Approximate expressions for T_{th} and θ are determined in both cases.

2. – Entropy flux in a solid subject to heating.

In order to explain the propagation of second sound in pure crystals at low temperatures, in [7, 8] it has been proposed a generalization of *Cattaneo* equation [4]. A different point of view has been considered in [22] using Rational Extended Thermodynamics [20]. Following this latter approach, the energy density E and the heat flux q_i are chosen as fundamental fields and for these

fields the following general balance equations are written:

$$(2.1) \quad \frac{\partial E}{\partial t} + \frac{\partial q_k}{\partial x_k} = 0,$$

$$(2.2) \quad \frac{\partial m_i}{\partial t} + \frac{\partial F_{ik}}{\partial x_k} = Q_i,$$

where m_i , F_{ik} and Q_i are quantities depending on the fundamental fields. A similar system of field equations is used in [1].

Since in system (2.1), (2.2) there are more unknowns than equations, it's necessary to complete it by adding *constitutive equations*, relating the variables m_i , F_{ik} and Q_i to independent fields E and q_i . Suppose that the fields m_i , F_{ik} and Q_i depend on fundamental fields in a manner such that the so-called *principle of frame indifference* is satisfied; i.e. the constitutive equations must be the same in all frames. Therefore, the constitutive quantities must be isotropic functions of their arguments, so that using the representation theorems for isotropic functions [21, 24], one can write:

$$(2.3) \quad m_i = \alpha(E, q^2) q_i, \quad F_{ij} = \beta(E, q^2) \delta_{ij} + \psi(E, q^2) q_i q_j, \quad Q_i = b(E, q^2) q_i,$$

where α , β , ψ and b are scalar functions. The coefficient α , playing the role of thermal inertia, has been introduced in [13, 22], whereas other authors [9, 10] take directly $\alpha = 1$; a possible physical meaning for this coefficient is proposed in [23].

In Rational Extended Thermodynamics, restrictions on constitutive relations (2.3) are obtained imposing the validity of entropy principle: there exist an entropy density h and an entropy flux Φ_k , which are both isotropic functions of E and q_i , i.e.

$$(2.4) \quad h = h(E, q^2), \quad \Phi_k = \phi(E, q^2) q_k,$$

such that the entropy production is supposed to be non-negative for every thermodynamic process, i.e.

$$(2.5) \quad \frac{\partial h}{\partial t} + \frac{\partial \Phi_k}{\partial x_k} \geq 0.$$

Remark that equations (2.1) and (2.2) can be considered as constraints for fields E and q_i . In order to satisfy entropy principle, a procedure, known as *Liu* method of Lagrange multipliers [14], will be used. It states that the following inequality

$$(2.6) \quad \frac{\partial h}{\partial t} + \frac{\partial \Phi_k}{\partial x_k} - \lambda_E \left[\frac{\partial E}{\partial t} + \frac{\partial q_k}{\partial x_k} \right] - \lambda_i \left[\frac{\partial m_i}{\partial t} + \frac{\partial F_{ik}}{\partial x_k} - Q_i \right] \geq 0$$

must be satisfied for arbitrary values of fields E and q_i . The quantities A_E and λ_i are the Lagrange multipliers, which are supposed also isotropic functions of fundamental fields; thus we can write:

$$(2.7) \quad A_E = A_E(E, q^2), \quad \lambda_i = \lambda(E, q^2) q_i.$$

The following proposition holds:

PROPOSITION 2.1. – *The most general constitutive function for the entropy flux compatible with entropy and material objectivity principles is furnished by the following expression:*

$$(2.8) \quad \Phi_k = A_E q_k + \frac{3}{2} \lambda_i F_{(ik)}.$$

PROOF. – Inserting constitutive relations (2.3) in inequality (2.6) a linear expression in the time and space derivatives of fundamental fields is obtained. In particular the coefficients of all derivatives must vanish. Putting zero the time derivatives of energy E and heat flux q_i , one obtains:

$$(2.9) \quad \left(\frac{\partial h}{\partial E} \right)_{q_i} = A_E + \lambda_i \frac{\partial m_i}{\partial E}, \quad \left(\frac{\partial h}{\partial q^2} \right)_E = \lambda_i \frac{\partial m_i}{\partial q^2},$$

from which one deduces

$$(2.10) \quad dh = A_E dE + \lambda_i dm_i.$$

Imposing that the coefficients of space derivatives E and q_i vanish, one finds:

$$(2.11) \quad \left(\frac{\partial \Phi_k}{\partial E} \right)_{q_i} = \lambda_i \frac{\partial F_{ik}}{\partial E}, \quad \left(\frac{\partial \Phi_k}{\partial q_j} \right)_E = A_E \frac{\partial q_i}{\partial q_j} + \lambda_i \frac{\partial F_{ik}}{\partial q_j},$$

from whence:

$$(2.12) \quad d\Phi_k = A_E dq_k + \lambda_i dF_{ik}.$$

Substituting (2.3)₂ in (2.11), one gets:

$$(2.13) \quad \left(\frac{\partial \phi}{\partial E} \right)_{q^2} = \lambda_q \left(\frac{\partial \beta}{\partial E} + \frac{2}{3} q^2 \frac{\partial \psi}{\partial E} \right),$$

$$(2.14) \quad \left(\frac{\partial \phi}{\partial q^2} \right)_E = \lambda \left(\frac{\partial \beta}{\partial q^2} + \frac{2}{3} q^2 \frac{\partial \psi}{\partial q^2} + \frac{1}{6} \psi \right),$$

and

$$(2.15) \quad \phi = A_E + \lambda\psi q^2;$$

from (2.13) and (2.14) finally one finds:

$$(2.16) \quad d\phi = \lambda \left[d\beta + \frac{2}{3} q^2 d\psi + \frac{1}{6} \psi dq^2 \right].$$

Substituting (2.15) in (2.4)₂ the following expression for the entropy flux is obtained:

$$(2.17) \quad \Phi_k = (A_E + \lambda\psi q^2) q_k.$$

The proof is completed observing that $\frac{3}{2} \lambda_i F_{(ik)} = \frac{3}{2} \lambda (\psi q_{(i} q_{k)}) q_i = \lambda \psi q^2 q_k$.

REMARK 2.1. – *The relation found shows that the entropy flux is known once the constitutive relations for Lagrange multipliers and for only traceless part of tensor F_{ik} have been determined.*

Denoting the coefficient linking entropy flux and heat flux with $\frac{1}{T_{th}}$, one has:

$$(2.18) \quad T_{th} = \frac{1}{A_E + \lambda\psi q^2}.$$

Recalling now that the non-equilibrium temperature has been defined as the inverse of partial derivative of entropy with respect to energy, at density and heat flux constant [10]:

$$(2.19) \quad \frac{1}{\theta} = \left(\frac{\partial h}{\partial E} \right)_{q_i} = A_E + \lambda q^2 \left(\frac{\partial \alpha}{\partial E} \right)_{q^2},$$

one obtains also:

$$(2.20) \quad \theta = \frac{1}{A_E + \lambda q^2 \alpha_E}$$

REMARK 2.2 $T_{th} = \theta \Leftrightarrow \psi = \alpha_E$. – *We conclude that thermodynamic temperature and non-equilibrium temperature can be identified, in general, only near equilibrium, when terms of second order in q_i can be neglected.*

2.1. *Approximate constitutive relations.*

In this subsection the attention is focused to processes far from equilibrium, considering constitutive relations for m_i and F_{ij} to fourth order in heat flux q_i , and for entropy h and entropy flux Φ_k to fifth order in heat flux. De-

note with \mathcal{Y} any of the quantities h , ϕ , α , β , ψ , \mathcal{A}_E and λ , put

$$(2.1.1) \quad \mathcal{Y} = \mathcal{Y}_0(E) + \mathcal{Y}_1(E) q^2 + \mathcal{Y}_2(E) q^4 + \mathcal{O}(q^6),$$

and observe from (2.10) that near equilibrium dh can be written as $dh_0 = \mathcal{A}_E^{(0)} dE$; therefore the energy Lagrange multiplier at equilibrium can be identified with the inverse of absolute equilibrium temperature T :

$$(2.1.2) \quad \mathcal{A}_E^{(0)} = \frac{1}{T}.$$

In this subsection the equilibrium temperature T will be used as independent variable instead of E . The simplified hypothesis $E = E(T)$ will be made. A prime will denote the derivative with respect to T .

Substituting (2.1.1) in expressions (2.10), (2.15) and (2.16), to the first order, one obtains:

$$(2.1.3) \quad h_0' = \frac{1}{T} E',$$

$$(2.1.4) \quad \phi_0 = \mathcal{A}_E^{(0)},$$

$$(2.1.5) \quad \phi_0' = \lambda_0 \beta_0';$$

using (2.1.2) from (2.1.5) one gets:

$$(2.1.6) \quad \beta_0' = -\frac{1}{T^2 \lambda_0}.$$

From which one obtains $\lambda_0 = \frac{\phi_0'}{\beta_0'}$, in accord with [22]. In this approximation, the entropy flux is $\Phi_k = \frac{1}{T} q_k$, as in classical thermodynamics.

To the second order in heat flux q_i , one obtains

$$(2.1.7) \quad h_1 = \frac{1}{2} \lambda_0 \alpha_0,$$

$$(2.1.8) \quad h_1' = \mathcal{A}_E^{(1)} E' + \lambda_0 \alpha_0',$$

$$(2.1.9) \quad \phi_1 = \lambda_0 \beta_1 + \frac{1}{6} \lambda_0 \psi_0,$$

$$(2.1.10) \quad \phi_1' = \lambda_0 \beta_1' + \frac{2}{3} \lambda_0 \psi_0' + \lambda_1 \beta_0';$$

comparing (2.1.9) with relation $\phi_1 = A_E^{(1)} + \lambda_0 \psi_0$ obtained by (2.15), one gets:

$$(2.1.11) \quad A_E^{(1)} = \lambda_0 \left(\beta_1 - \frac{5}{6} \psi_0 \right).$$

From (2.1.7) and (2.1.8) one obtains:

$$(2.1.12) \quad \frac{1}{2} (\lambda_0 \alpha_0)' - \lambda_0 \alpha_0' = A_E^{(1)} E',$$

and then

$$(2.1.13) \quad \alpha_0(T) = \lambda_0 \left(c_1 - 2 \int_{T_0}^T \frac{A_E^{(1)}}{\lambda_0^2} E' d\xi \right);$$

with $c_1 = \frac{\alpha_0(T_0)}{\lambda_0(T_0)}$. When $A_E^{(1)} = 0$, one recovers the result of [22].

From (2.1.9), (2.1.10) and (2.1.11) one obtains:

$$(2.1.14) \quad \lambda_0^2 \psi_0' - 2\lambda_0 \lambda_0' \psi_0 = 2(\lambda_0' A_E^{(1)} - \lambda_0 \lambda_1 \beta_0'),$$

and then

$$(2.1.15) \quad \psi_0(T) = \lambda_0^2 \left(c_2 + 2 \int_{T_0}^T \frac{\lambda_0' A_E^{(1)} - \lambda_0 \lambda_1 \beta_0'}{\lambda_0^4} d\xi \right);$$

with $c_2 = \frac{\psi_0(T_0)}{\lambda_0^2(T_0)}$. From (2.1.11), the knowledge of $A_E^{(1)}$ furnishes β_1 .

From (2.1.7) and (2.1.13) one has:

$$(2.1.16) \quad h_1 = \frac{1}{2} \lambda_0^2 \left(c_1 - 2 \int_{T_0}^T \frac{A_E^{(1)}}{\lambda_0^2} E' d\xi \right),$$

$$(2.1.17) \quad \phi_1 = A_E^{(1)} + \lambda_0^3 \left(c_2 + 2 \int_{T_0}^T \frac{\lambda_0' A_E^{(1)} - \lambda_0 \lambda_1 \beta_0'}{\lambda_0^4} d\xi \right).$$

To fourth order in heat flux q_i one obtains:

$$(2.1.18) \quad h_2 = \frac{1}{4} (3\lambda_0 \alpha_1 + \lambda_1 \alpha_0),$$

$$(2.1.19) \quad h_2' = A_E^{(2)} E' + \lambda_0 \alpha_1' + \lambda_1 \alpha_0',$$

$$(2.1.20) \quad \phi_2 = \frac{1}{2} \left(\lambda_1 \beta_1 + \frac{5}{6} \lambda_0 \psi_1 + \frac{1}{6} \lambda_1 \psi_0 \right) + \lambda_0 \beta_2,$$

$$(2.1.21) \quad \phi_2' = \lambda_1 \beta_1' + \frac{2}{3} \lambda_0 \psi_1' + \frac{2}{3} \lambda_1 \psi_0' + \lambda_0 \beta_2' + \lambda_2 \beta_0'.$$

and

$$(2.1.22) \quad \phi_2 = A_E^{(2)} + \lambda_0 \psi_1 + \lambda_1 \psi_0.$$

Comparing (2.1.22) and (2.1.19) one obtains:

$$(2.1.23) \quad A_E^{(2)} = \frac{1}{2} \lambda_1 \beta_1 - \frac{7}{12} \lambda_0 \psi_1 - \frac{11}{12} \lambda_1 \psi_0 + \lambda_0 \beta_2.$$

From (2.1.18) and (2.1.19) the following linear ordinary differential equation in unknown α_1 is obtained:

$$(2.1.24) \quad \lambda_0 \alpha_1' - 3\lambda_0' \alpha_1 = \lambda_1' \alpha_0 - 3\lambda_1 \alpha_0' - 4A_E^{(2)} E',$$

and then

$$(2.1.25) \quad \alpha_1(T) = \lambda_0^3 \left(c_3 + \int_{T_0}^T \frac{\lambda_1' \alpha_0 - 3\lambda_1 \alpha_0' - 4A_E^{(2)} E'}{\lambda_0^4} d\xi \right)$$

with $c_3 = \frac{\alpha_1(T_0)}{\lambda_0^3(T_0)}$. To the fourth order in heat flux q_i , the entropy flux can be written:

$$(2.1.26) \quad \Phi_k = \left[\frac{1}{T} + \lambda_0 \left(\beta_1 + \frac{1}{6} \psi_0 \right) q^2 + \left(\lambda_0 \left(\beta_2 + \frac{5}{12} \psi_1 \right) + \lambda_1 \left(\frac{1}{2} \beta_1 + \frac{1}{12} \psi_0 \right) \right) q^4 \right] q_k + \mathcal{O}(q^6).$$

Finally, the following approximate expressions for thermodynamic temperature T_{th} and for non-equilibrium temperature θ are obtained:

$$(2.1.27) \quad T_{th} = T - \lambda_0 T^2 \left(\beta_1 + \frac{1}{6} \psi_0 \right) q^2 + \\ - 2T^2 \left(\frac{1}{2} \lambda_1 \beta_1 + \frac{5}{12} \lambda_0 \psi_1 + \frac{1}{12} \lambda_1 \psi_0 + \lambda_0 \beta_2 \right) q^4 + \\ + \lambda_0 T^3 \left(\beta_1 + \frac{1}{6} \psi_0 \right) q^4 + \mathcal{O}(q^6),$$

$$(2.1.28) \quad \theta = T - \lambda_0 T^2 \left(\beta_1 - \frac{5}{6} \psi_0 + \frac{\alpha_0'}{E'} \right) q^2 + \\ - 2T^2 \left(\frac{1}{2} \lambda_1 \beta_1 - \frac{7}{12} \lambda_0 \psi_1 - \frac{11}{12} \lambda_1 \psi_0 + \lambda_0 \beta_2 + \frac{\lambda_0 \alpha_1' + \lambda_1 \alpha_0'}{E'} \right) q^4 + \\ + \lambda_0 T^3 \left(\beta_1 - \frac{5}{6} \psi_0 + \frac{\alpha_0'}{E'} \right) q^4 + \mathcal{O}(q^6),$$

from which

$$(2.1.29) \quad T_{th} - \theta = -\lambda_0 T^2 \left(\psi_0 - \frac{\alpha'_0}{E'} \right) q^2 + \\ - \left[2T^2 \left(\lambda_0 \psi_1 + \lambda_1 \psi_0 - \frac{\lambda_0 \alpha'_1 + \lambda_1 \alpha'_0}{E'} \right) + \lambda_0 T^3 \left(\psi_0 - \frac{\alpha'_0}{E'} \right) \right] q^4 + \mathcal{O}(q^6).$$

3. – Entropy flux in a non viscous gas subject to heating.

The behavior of fluids and gases in the presence of high values of heat flux has been in recent years the object of many investigations. Many materials require the use of the heat flux as an independent variable for their description: superfluids, hydrodynamical models for the charge transport inside semiconductors, hydrodynamics of phonons and photons, plasmas, ultrarelativistic fluids, etc. (see the bibliography in [9, 10], [18]-[20]). The approximation to assume the hypothesis of zero-viscosity in gases may be useful [17], and in E.T. this hypothesis means to set equal to zero the evolution time of non-equilibrium part of pressure tensor.

In this section, using Rational Extended Thermodynamics the complete expression of entropy flux in a dilute non viscous gas will be determined, i.e. a gas whose evolution time of heat flux is high, while the evolution time of stress deviator is zero.

The behavior of a dilute gas can be described by the following balance equations [20]:

$$(3.1) \quad \frac{\partial \varrho_A}{\partial t} + \frac{\partial \varrho_{Ak}}{\partial x_k} = P_A \quad (A = ., i, ij, ijk, \dots)$$

In these equations, the quantities ϱ_A are the moments of various order of phase density of kinetic theory of gases [6], ϱ_{Ak} are the fluxes of fields ϱ_A , which in this theory are just the moments of successive order, P_A are the production terms. In the following the gas will be supposed in an inertial frame, and in absence of external forces.

In Extended Thermodynamics of ideal and real gases the central moments are often chosen as independent fields instead of complete moments. Denoting with f the phase-density function, with m the atomic mass and with c_i the peculiar velocity, the central moment $\widehat{Q}_{ijk\dots l}$ is defined as [6]:

$$(3.2) \quad \widehat{Q}_{ijk\dots l} = \int m c_i c_j c_k \dots c_l f dc .$$

This paper deals with balance equations for the first 13 moments ϱ , ϱ_i , ϱ_{ij} , ϱ_{ijj}

only. Total moments are expressed easily as functions of central moments, in the following way [6],

$$(3.3) \quad \varrho = \widehat{\varrho},$$

$$(3.4) \quad \varrho_i = \widehat{\varrho} v_i = \varrho v_i,$$

$$(3.5) \quad \varrho_{ij} = \widehat{\varrho}_{ij} + \varrho v_i v_j,$$

$$(3.6) \quad \varrho_{ijk} = \widehat{\varrho}_{ijk} + 3 \widehat{\varrho}_{(ij} v_k) + \varrho v_i v_j v_k,$$

$$(3.7) \quad \varrho_{ijkl} = \widehat{\varrho}_{ijkl} + 4 \widehat{\varrho}_{(ijk} v_l) + 6 \widehat{\varrho}_{(ij} v_k v_l) + \varrho v_i v_j v_k v_l,$$

Insertion of these relations into balance equations for first 13 moments leads to:

$$(3.8) \quad \left\{ \begin{array}{l} \dot{\varrho} + \varrho \frac{\partial v_k}{\partial x_k} = 0, \\ \varrho \dot{v}_i + \frac{\partial p_{ik}}{\partial x_k} = 0, \\ \dot{E} + E \frac{\partial v_k}{\partial x_k} + \frac{\partial q_k}{\partial x_k} + p_{ik} \frac{\partial v_i}{\partial x_k} = 0, \\ \dot{p}_{(ik)} + p_{(ik)} \frac{\partial v_j}{\partial x_j} + \frac{\partial}{\partial x_j} \left(\frac{4}{5} q_{(i} \delta_{k)j} + \widehat{\varrho}_{(ijk)} \right) + 2 p_{j(i} \frac{\partial v_k)}{\partial x_j} = \widehat{P}_{(ik)}, \\ \dot{q}_i + q_i \frac{\partial v_k}{\partial x_k} + q_k \frac{\partial v_i}{\partial x_k} + \widehat{\varrho}_{ijk} \frac{\partial v_j}{\partial x_k} + \frac{1}{2} \frac{\partial \widehat{\varrho}_{ijk}}{\partial x_k} - \frac{3}{2\varrho} p_{(ij} \frac{\partial p_{j)k}}{\partial x_k} = \frac{1}{2} \widehat{P}_{ill}. \end{array} \right.$$

In this system we have put $p_{ij} = \widehat{\varrho}_{ij}$; $E = \frac{1}{2} p_{ll}$ is the internal energy density, $p_{(ij)}$ the deviatoric part of stress tensor p_{ij} and $q_i = \frac{1}{2} \widehat{\varrho}_{lli}$ heat flux. In this theory the trace of stress $\widehat{p}_{ll} = 3p$ (p is the pressure) is linked to internal energy density E by the relation: $3p = 2E$.

In order to describe, with a sufficient approximation, the behavior of a given material using extended thermodynamics, it is not necessary to consider all 13 moments ϱ_A as fundamental fields, but it could be sufficient to maintain only those whose evolution times are relatively slow. For instance, the evolution of an ordinary fluid may be described using the moments ϱ , ϱ_i and ϱ_{ll} : mass density, momentum density and energy density respectively. In the presence of high values of heat flux, if one supposes high the evolution time of heat flux and zero the evolution time of stress deviator only density ϱ , velocity v_i , internal energy density E and heat flux q_i can be used as fundamental fields. As it has been shown in [16], this is equivalent to suppose zero the intrinsic Lagrange multiplier $\widehat{\Lambda}_{(ij)}$ of stress deviator $p_{(ij)}$. The evolution equa-

tions for these fields can be obtained from (3.8) neglecting the evolution equation of stress deviator; we obtain:

$$(3.9) \quad \left\{ \begin{aligned} \dot{\varrho} + \varrho \frac{\partial v_k}{\partial x_k} &= 0, \\ \varrho \dot{v}_i + \frac{\partial p_{ik}}{\partial x_k} &= 0, \\ \dot{E} + E \frac{\partial v_k}{\partial x_k} + \frac{\partial q_k}{\partial x_k} + p_{ik} \frac{\partial v_i}{\partial x_k} &= 0, \\ \dot{q}_i + q_i \frac{\partial v_k}{\partial x_k} + q_k \frac{\partial v_i}{\partial x_k} + \widehat{Q}_{ijk} \frac{\partial v_j}{\partial x_k} + \frac{1}{2} \frac{\partial \widehat{Q}_{ijk}}{\partial x_k} - \frac{3}{2\varrho} p_{(ij} \frac{\partial p_{j)k}}{\partial x_k} &= \frac{1}{2} \widehat{P}_{ill}. \end{aligned} \right.$$

Assuming the validity of material objectivity principle, the constitutive equations for non fundamental fields $p_{(ik)}$, \widehat{Q}_{ijk} and \widehat{Q}_{ijk} can be expressed in the form:

$$(3.10) \quad p_{ij} = \frac{2}{3} E \delta_{ij} + a(\varrho, E, q^2) q_{(i} q_{j)},$$

$$(3.11) \quad \widehat{Q}_{ijk} = \frac{2}{5} (q_i \delta_{jk} + q_j \delta_{ki} + q_k \delta_{ij}) + \chi(\varrho, E, q^2) q_{(i} q_j q_{k)},$$

$$(3.12) \quad \widehat{Q}_{ijk} = \beta(\varrho, E, q^2) \delta_{ik} + \nu(\varrho, E, q^2) q_{(i} q_{k)},$$

where a, χ, β and ν are scalar functions.

Restrictions on the constitutive relations (3.10, 3.11, 3.12) are obtained using entropy principle, i.e. imposing that the following inequality is satisfied for every thermodynamic process:

$$(3.13) \quad \dot{h} + h \frac{\partial v_k}{\partial x_k} + \frac{\partial \Phi_k}{\partial x_k} \geq 0.$$

In this inequality, h and Φ_k are objective functions of fundamental fields:

$$(3.14) \quad h = h(\varrho, E, q^2), \quad \Phi_k = \phi(\varrho, E, q^2) q_k.$$

The following proposition holds:

PROPOSITION 3.1. – *The most general constitutive function for the entropy flux compatible with entropy principle and material objectivity principle is furnished by the following expression:*

$$(3.15) \quad \Phi_k = \left[\widehat{\Lambda}_E + \widehat{\lambda} \left(\frac{\nu}{2} - aG \right) q^2 \right] q_k.$$

where we have put $G = \frac{5E + 2aq^2}{3\varrho}$; $\widehat{\Lambda}_E$ and $\widehat{\lambda}$ are the non convective parts of Lagrange multipliers of energy and of heat flux respectively [19, 20].

PROOF. – Applying Liu method of Lagrange multipliers, the following inequality is obtained:

$$(3.16) \quad \dot{h} + h \frac{\partial v_k}{\partial x_k} + \frac{\partial \Phi_k}{\partial x_k} - \widehat{\Lambda} \left[\dot{q} + \varrho \frac{\partial v_k}{\partial x_k} \right] - \\ \widehat{\Lambda}_i \left[\dot{v}_i + \frac{1}{\varrho} \frac{\partial p_{ik}}{\partial x_k} \right] - \widehat{\Lambda}_E \left[\dot{E} + E \frac{\partial v_k}{\partial x_k} + \frac{\partial q_k}{\partial x_k} + p_{ik} \frac{\partial v_i}{\partial x_k} \right] - \\ \widehat{\lambda}_i \left[\dot{q}_i + q_i \frac{\partial v_k}{\partial x_k} + q_k \frac{\partial v_i}{\partial x_k} + \widehat{Q}_{ijk} \frac{\partial v_j}{\partial x_k} + \right. \\ \left. \frac{1}{2} \frac{\partial \widehat{Q}_{ijk}}{\partial x_k} - \frac{3}{2\varrho} p_{(ij)} \frac{\partial p_{j)k}}{\partial x_k} - \frac{1}{2} \widehat{P}_{ill} \right] \geq 0.$$

The quantities $\widehat{\Lambda}$, $\widehat{\Lambda}_i$, $\widehat{\Lambda}_E$ and $\widehat{\lambda}_i$ are the non convective parts of Lagrange multipliers, which are also objective functions, so that we can write $\widehat{\Lambda} = \widehat{\Lambda}(\varrho, E, q^2)$, $\widehat{\Lambda}_i = \widehat{\Lambda}_i(\varrho, E, q^2) q_i$, $\widehat{\Lambda}_E = \widehat{\Lambda}_E(\varrho, E, q^2)$, $\widehat{\lambda}_i = \widehat{\lambda}(\varrho, E, q^2) q_i$.

As shown in [17, 18], imposing zero the coefficients of time and space derivatives one obtains:

$$(3.17) \quad \widehat{\Lambda}_v = 0, \quad dh = \widehat{\Lambda} d\varrho + \widehat{\Lambda}_E dE + \widehat{\lambda}_i dq_i.$$

$$(3.18) \quad h - \varrho \widehat{\Lambda} - \frac{5}{3} \widehat{\Lambda}_E E - 2 \widehat{\lambda} q^2 = 0, \quad a \widehat{\Lambda}_E + \widehat{\lambda} \frac{9 + 3\chi q^2}{5} = 0.$$

$$(3.19) \quad d\Phi_k = \widehat{\Lambda}_E dq_k + \widehat{\lambda}_i \left(\frac{1}{2} d\widehat{Q}_{ijk} - \frac{3}{2\varrho} p_{(ij)} dp_{j)k} \right).$$

From (3.19) one can write:

$$(3.20) \quad \phi - \widehat{\Lambda}_E - \widehat{\lambda} q^2 \left[\frac{\nu}{2} - aG \right] = 0,$$

$$(3.21) \quad d\phi = \widehat{\lambda} \left[\frac{1}{2} d\beta + \frac{1}{3} q^2 d\nu + \frac{1}{6} \left(\frac{\nu}{2} - aG \right) dq^2 - \frac{1}{6} G(4dE + 4q^2 da) \right].$$

Using (3.14)₂ and (3.20), equation (3.15) is obtained.

REMARK 3.1. - Denoting with $\frac{1}{T_{th}}$ the coefficient linking Φ_k and q_k , one obtains:

$$(3.22) \quad T_{th} = \frac{1}{\widehat{\Lambda}_E + \widehat{\lambda} q^2 \left[\frac{\nu}{2} - aG \right]},$$

while $\theta = \frac{1}{\Lambda_E}$.

3.1. Approximate constitutive relations.

In this subsection only processes near equilibrium will be considered. Denote with Y any of the 9 quantities $h, \phi, \alpha, \beta, \nu, \chi, \widehat{\Lambda}, \widehat{\Lambda}_U$ and $\widehat{\lambda}$, and put:

$$(3.1.1) \quad Y = Y_0(\varrho, E) + Y_1(\varrho, E)q^2 + \mathcal{O}(q^4).$$

Neglecting terms of order greater than 3 with respect to q , a set of relations are obtained: the following relations involving only constitutive quantities:

$$(3.1.2) \quad 2h_1 - \widehat{\lambda}_0 = 0,$$

$$(3.1.3) \quad h_0 - \varrho \widehat{\Lambda}_0 - \frac{5}{3} E \widehat{\Lambda}_E^0 = 0,$$

$$(3.1.4) \quad \phi_0 - \widehat{\Lambda}_E^0 = 0,$$

$$(3.1.5) \quad 4h_2 - \widehat{\lambda}_1 = 0,$$

$$(3.1.6) \quad a_0 \widehat{\Lambda}_E^0 + \frac{9}{5} \widehat{\lambda}_0 = 0,$$

$$(3.1.7) \quad h_1 - \varrho \widehat{\Lambda}_1 - \frac{5}{3} E \widehat{\Lambda}_E^1 - 2 \widehat{\lambda}_0 = 0,$$

$$(3.1.8) \quad 2\phi_1 - \widehat{\lambda}_0 \left[\beta_1 + \frac{1}{6} \nu_0 - \frac{5E}{9\varrho} a_0 \right] = 0,$$

$$(3.1.9) \quad 5\phi_1 - 3 \widehat{\Lambda}_E^1 - \widehat{\lambda}_0 \left(\beta_1 + \frac{5}{3} \nu_0 - \frac{50E}{9\varrho} a_0 \right) = 0,$$

and the following differential relations:

$$(3.1.10) \quad dh_0 = \widehat{\Lambda}_0 d\varrho + \widehat{\Lambda}_E^0 dE,$$

$$(3.1.11) \quad d\phi_0 = \widehat{\lambda}_0 \left[\frac{1}{2} d\beta_0 - \frac{10E}{9\varrho} dE \right],$$

$$(3.1.12) \quad dh_1 = \widehat{\Lambda}_1 d\varrho + \widehat{\Lambda}_E^{(1)} dE,$$

$$(3.1.13) \quad d\phi_1 = \widehat{\lambda}_0 \left(\frac{1}{2} d\beta_1 + \frac{1}{3} d\nu_0 - \frac{4}{9\varrho} a_0 dE - \frac{10}{9\varrho} E d a_0 \right) + \\ \widehat{\lambda}_1 \left(\frac{1}{2} d\beta_0 - \frac{10}{9\varrho} E dE \right).$$

Equation (3.1.10) can be written:

$$(3.1.14) \quad d \left(\frac{h_0}{\varrho} \right) = \widehat{\Lambda}_E^0 \left[d \left(\frac{E}{\varrho} \right) - \frac{p}{\varrho^2} d\varrho \right].$$

Denoting with $\eta_0 = h_0/\varrho$ and $\varepsilon = E/\varrho$ the equilibrium specific entropy and the specific internal energy respectively, and identifying $\widehat{\Lambda}_E^0$ with the inverse of absolute equilibrium temperature T , the Gibbs equation of thermostatic is obtained:

$$(3.1.15) \quad d\eta = \frac{1}{T} \left[d\varepsilon - \frac{p}{\varrho^2} d\varrho \right].$$

From this relation, reasoning as in [15], we deduce that the state equation must have the form:

$$(3.1.16) \quad p = T^{5/2} F(z) \quad \text{with} \quad z = \frac{\varrho}{T^{3/2}}.$$

By (3.1.4) one obtains $\phi_0 = \frac{1}{T}$; substituting in (3.1.11) one gets:

$$(3.1.17) \quad d \left(\frac{1}{T} \right) = \widehat{\lambda}_0 \left(\frac{1}{2} d\beta_0 - \frac{5}{3} \varepsilon dp \right),$$

which yields the following integrability conditions:

$$(3.1.18) \quad \frac{1}{2} \frac{\partial \beta_0}{\partial \varrho} - \frac{5}{3} \varepsilon \frac{\partial p}{\partial \varrho} = 0, \quad \frac{1}{2} \frac{\partial \beta_0}{\partial T} - \frac{5}{3} \varepsilon \frac{\partial p}{\partial T} = -\frac{1}{T^2 \widehat{\lambda}_0}.$$

Putting:

$$(3.1.19) \quad \zeta = \frac{1}{2} \frac{\partial \beta_0}{\partial T} - \frac{5}{3} \varepsilon \frac{\partial p}{\partial T},$$

one can write:

$$(3.1.20) \quad \widehat{\lambda}_0 = -\frac{1}{T^2 \zeta}, \quad h_1 = -\frac{1}{2T^2 \zeta},$$

$$(3.1.21) \quad a_0 = -\frac{9\lambda_0}{5\widehat{\Lambda}_E^0} = \frac{9}{5T\zeta}, \quad \phi_1 = -\frac{1}{4T^2 \zeta} \left(2\beta_1 + \frac{1}{3} \nu_0 - \frac{3p}{\varrho T \zeta} \right).$$

Substituting this latter quantity in (3.14) one gets the following expression of entropy flux approximate to third order in q_i ,

$$(3.1.22) \quad \Phi_k = \left(\frac{1}{T} - \frac{1}{4T^2\xi} \left(2\beta_1 + \frac{1}{3}\nu_0 - \frac{3p}{\rho T\xi} \right) q^2 \right) q_k + \mathcal{O}(q^4).$$

Finally, the following relation between thermodynamic temperature and non-equilibrium temperature is obtained:

$$(3.1.23) \quad T_{th} - \theta = -\hat{\lambda}_0 T \left(\frac{\nu_0}{2} - \frac{5a_0}{3\rho} E \right) q^2 + \mathcal{O}(q^4),$$

which shows that also in a non viscous dilute gas the thermodynamic temperature do not coincide with the non-equilibrium temperature θ .

REFERENCES

- [1] A. M. ANILE - S. PENNISI - M. SAMMARTINO, *A thermodynamical approach to Ed-dington factors*, J. Math. Phys., **32** (2), (1991), 544-550.
- [2] J. AU - I. MÜLLER - T. RUGGERI, *Temperature jumps at the boundary of a rarified gas*, Continuum Mech. Thermodyn., **12** (2000), 19-29.
- [3] E. BARBERA - I. MÜLLER - M. SUGIYAMA, *On the temperatures of a rarefied gas in non-equilibrium*, Meccanica, **34** (1999), 103-113.
- [4] C. CATTANEO, *Sulla conduzione del calore*, Atti Sem. Mat. Fis. Univ. Modena, **3** (1948), 83-101.
- [5] R. DOMINGUEZ-CASCANTE - D. JOU, *Entropy Flux and Absolute temperature in Extended Irreversible Thermodynamics*, J. Non-Equilib. Thermodyn., **20** (1995), 263-273.
- [6] H. GRAD, *Principles of the kinetic theory of gases*, Handbuch der Physik XII, Thermodynamik der Gase, Springer-Verlag, Berlin (1958), 205-294.
- [7] R. A. GUYER - J. A. KRUMHANSL, *Solution of the linearized phonon Boltzmann equation*, Phys. Rev., **148** (2), (1966), 766-778.
- [8] R. A. GUYER - J. A. KRUMHANSL, *Thermal conductivity, second sound and phonon hydrodynamic phenomena in nonmetal crystals*, Phys. Rev., **148** (2), (1966), 778-788.
- [9] D. JOU - J. CASAS-VÁZQUEZ - G. LEBON, *Extended Irreversible Thermodynamics revisited (1988-1998)*, Rep. Prog. Phys., **62** (1999), 1035-1142.
- [10] D. JOU - J. CASAS-VÁZQUEZ - G. LEBON, *Extended Irreversible Thermodynamics*, Springer-Verlag, Berlin (2001).
- [11] D. JOU - J. CASAS-VÁZQUEZ, *Possible experiment to check the reality of a nonequilibrium temperature*, Phys. Rev. A, **45** (12), (1992), 8371-8373.
- [12] J. CASAS-VÁZQUEZ - D. JOU, *Nonequilibrium temperature versus local-equilibrium temperature*, Phys. Rev. E, **49** (2) (1994), 1040-1048.
- [13] G. M. KREMER, *On extended thermodynamics of ideal and real gases*, Extended Thermodynamics Systems, Sieniutycz S. and Salamon P. editors, Taylor and Francis (1992), 140-182.

- [14] I. LIU, *Method of Lagrange multipliers for exploitation of the entropy principle*, Arch. Rat. Mech. Anal., **46** (1972), 131-148.
- [15] I. LIU - I. MÜLLER, *Extended Thermodynamics of classical and degenerate gases*, Arch. Rat. Mech. Anal., **83** (4) (1983), 285-332.
- [16] M. S. MONGIOVÌ, *Some considerations about Nonlinear Extended Thermodynamic Theories with different number of fields*, J. Non-Equilib. Thermodyn., **24** (1999), 147-153.
- [17] M. S. MONGIOVÌ, *Thermodynamic pressure in nonlinear nonequilibrium thermodynamics of dilute nonviscous gases*, Phys. Rev. E, **63** (2001), 1-4.
- [18] M. S. MONGIOVÌ, *Non-linear Non-viscous Hydrodynamical Models for Charge Transport in the framework of Extended Thermodynamic methods*, Math. Comp. Modelling, **35** (2002), 813-820.
- [19] M. S. MONGIOVÌ, *Nonlinear Extended Thermodynamics of a Dilute Nonviscous Gas*, Math. Comp. Modelling, **36** (2002), 951-962.
- [20] I. MÜLLER - T. RUGGERI, *Rational Extended Thermodynamics*, Springer-Verlag, Berlin (1998).
- [21] G. F. SMITH, *On isotropic Integrity Bases*, Arch.Rat.Mech.Anal., **18**, (1965), 282-292.
- [22] T. RUGGERI - A. MURACCHINI - L. SECCIA, *Continuum approach to Phonon Gas and Shape Changes of Second Sound via Shock Waves Theory*, Il Nuovo Cimento D, **16** (1), (1994), 15-44.
- [23] A. VALENTI - M. TORRISI - G. LEBON, *Shock Waves in Crystalline Dielectrics at Low Temperature*, J. Phys.: Condens.Matter, **14** (2002), 3553-3564.
- [24] C. C. WANG, *A new representation theorem for isotropic functions*, Arch. Rat. Mech. Anal., **36** (1970), 166-197.

M. S. Mongiovi: Facoltà di Ingegneria, viale Delle Scienze
e-mail: mongiovi@unipa.it

R. A. Peruzza: Facoltà di Scienze MM.FF.NN., via Archirafi 34
e-mail: peruzza@math.unipa.it