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

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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 $\theta$ 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 $\theta$ are determined in both cases.

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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 $\theta$ 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 $\theta$ 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:

\[
\begin{align*}
\frac{\partial E}{\partial t} + \frac{\partial q_k}{\partial x_k} &= 0, \\
\frac{\partial m_i}{\partial t} + \frac{\partial F_{ik}}{\partial x_k} &= Q_i,
\end{align*}
\]

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:

\[
\begin{align*}
m_i &= \alpha(E, q) q_i, \\
F_{ij} &= \beta(E, q) \delta_{ij} + \psi(E, q^2) q_i q_j, \\
Q_i &= b(E, q^2) q_i,
\end{align*}
\]

where \(\alpha, \beta, \psi\) and \(b\) are scalar functions. The coefficient \(\alpha\), 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 \(\Phi_k\), which are both isotropic functions of \(E\) and \(q_i\), i.e.

\[
\begin{align*}
h &= h(E, q^2), \\
\Phi_k &= \phi(E, q^2) q_k,
\end{align*}
\]

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

\[
\frac{\partial h}{\partial t} + \frac{\partial \Phi_k}{\partial x_k} \geq 0.
\]

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

\[
\begin{align*}
\frac{\partial h}{\partial t} + \frac{\partial \Phi_k}{\partial x_k} - \Lambda_E \left[ \frac{\partial E}{\partial t} + \frac{\partial q_k}{\partial x_k} \right] - \lambda_i \left[ \frac{\partial m_i}{\partial t} + \frac{\partial F_{ik}}{\partial x_k} - Q_i \right] \geq 0,
\end{align*}
\]
must be satisfied for arbitrary values of fields \( E \) and \( q_i \). The quantities \( \Lambda_E \) and \( \lambda_i \) are the Lagrange multipliers, which are supposed also isotropic functions of fundamental fields; thus we can write:

\[
\Lambda_E = \Lambda_E(E, q^2), \quad \lambda_i = \lambda(E, q^2) q_i. \tag{2.7}
\]

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:

\[
\Phi_k = \Lambda_E q_k + \frac{3}{2} \lambda_i F_{(ik)}. \tag{2.8}
\]

**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:

\[
\left( \frac{\partial h}{\partial E} \right)_q = \Lambda_E + \lambda_i \frac{\partial m_i}{\partial E}, \quad \left( \frac{\partial h}{\partial q^2} \right)_E = \lambda_i \frac{\partial m_i}{\partial q^2}, \tag{2.9}
\]

from which one deduces

\[
\partial h = \Lambda_E dE + \lambda_i dm_i. \tag{2.10}
\]

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

\[
\left( \frac{\partial \Phi_k}{\partial E} \right)_{q_i} = \lambda_i \frac{\partial F_{ik}}{\partial E}, \quad \left( \frac{\partial \Phi_k}{\partial q_j} \right)_E = \Lambda_E \frac{\partial q_i}{\partial q_j} + \lambda_i \frac{\partial F_{ik}}{\partial q_j}, \tag{2.11}
\]

from whence:

\[
d\Phi_k = \Lambda_E dq_k + \lambda_i dF_{ik}. \tag{2.12}
\]

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

\[
\left( \frac{\partial \phi}{\partial E} \right)_{q^2} = \lambda q \left( \frac{\partial \beta}{\partial E} + \frac{2}{3} q^2 \frac{\partial \psi}{\partial E} \right), \tag{2.13}
\]

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

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

one obtains also:

\[(2.20) \quad \theta = \frac{1}{A_E + \lambda q^2 a_E} \]

**Remark 2.2** \(T_{th} = \theta \iff \psi = a_E.\) – 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 \(\Phi_k\) to fifth order in heat flux. De-
note with $r$ any of the quantities $h$, $\phi$, $\alpha$, $\beta$, $\psi$, $A_E$ and $\lambda$, put

\begin{equation}
(2.1.1) \quad r = r_0(E) + r_1(E) q^2 + r_2(E) q^4 + \mathcal{O}(q^6),
\end{equation}

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

\begin{equation}
(2.1.2) \quad A_E^{(0)} = \frac{1}{T}.
\end{equation}

In this subsection the equilibrium temperature $T$ will be used as independent variable instead of $E$. The symplified hypothesis $E = E(T)$ will be made. A prime will be 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:

\begin{align}
(2.1.3) \quad & h_0' = \frac{1}{T} E', \\
(2.1.4) \quad & \phi_0 = A_E^{(0)}, \\
(2.1.5) \quad & \phi_0' = \lambda_0 \beta_0';
\end{align}

using (2.1.2) from (2.1.5) one gets:

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

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

\begin{align}
(2.1.7) \quad & h_1 = \frac{1}{2} \lambda_0 \alpha_0, \\
(2.1.8) \quad & h_1' = 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';
\end{align}
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

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

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:

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

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 $\beta_1$.

From (2.1.7) and (2.1.13) one has:

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

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

To fourth order in heat flux $q_i$ one obtains:

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

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

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

\[(2.1.21) \quad \phi_2 = \lambda_1 \beta_1' + \frac{2}{3} \lambda_0 \psi_1' + \frac{2}{3} \lambda_1 \psi_0' + \lambda_0 \beta_2' + \lambda_2 \beta_0'. \]
Comparing (2.1.22) and (2.1.19) one obtains:

\[ \phi_2 = \phi_0^{(2)} + \lambda_0 \psi_1 + \lambda_1 \psi_0. \]

From (2.1.18) and (2.1.19) the following linear ordinary differential equation in unknown \( \alpha_1 \) is obtained:

\[ \lambda_0 \alpha_1' - 3 \lambda_2 \alpha_1 = \lambda_1' \alpha_0 - 3 \lambda_1 \alpha_0' - 4 \phi_0^{(2)} E', \]

and then

\[ \alpha_1(T) = \left( c_3 + \int_{T_0}^{T} \frac{\lambda_1' \alpha_0 - 3 \lambda_1 \alpha_0' - 4 \phi_0^{(2)} E'}{\lambda_0^2} \, d\xi \right) \]

with \( c_3 = \frac{\alpha_1(T_0)}{\lambda_0^2(T_0)} \). To the fourth order in heat flux \( q_i \), the entropy flux can be written:

\[ \Phi_k = \left[ \frac{1}{T} + \lambda_0 \left( \beta_1 + \frac{1}{6} \psi_0 \right) q^2 + \right. \]

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

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

\[ T_{th} = T - \lambda_0 T^2 \left( \beta_1 + \frac{1}{6} \psi_0 \right) q^2 + \]

\[ -2 T^2 \left( \frac{1}{2} \lambda_1 \beta_1 + \frac{5}{12} \lambda_0 \psi_1 + \frac{1}{12} \lambda_1 \psi_0 + \lambda_0 \beta_2 \right) q^4 + \]

\[ + \lambda_0 T^3 \left( \beta_1 + \frac{1}{6} \psi_0 \right) q^4 + O(q^6), \]

\[ \theta = T - \lambda_0 T^2 \left( \beta_1 - \frac{5}{6} \psi_0 + \frac{\alpha'_0}{E'} \right) q^2 + \]

\[ -2 T^2 \left( \frac{1}{2} \lambda_1 \beta_1 - \frac{7}{12} \lambda_0 \psi_1 - \frac{11}{12} \lambda_1 \psi_0 + \lambda_0 \beta_2 + \frac{\lambda_0 \alpha'_0 + \lambda_1 \alpha'_0}{E'} \right) q^4 + \]

\[ + \lambda_0 T^3 \left( \beta_1 - \frac{5}{6} \psi_0 + \frac{\alpha'_0}{E'} \right) q^4 + O(q^6), \]
from which

\begin{equation}
(2.1.29) \quad T_{th} - \theta = -\lambda_0 T^2 \left( \psi_0 - \frac{\alpha_0'}{E'} \right) q^2 + \left[ 2 T^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 + O(q^6) .
\end{equation}

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]:

\begin{equation}
(3.1) \quad \frac{\partial Q_A}{\partial t} + \frac{\partial Q_{Ak}}{\partial x_k} = P_A \quad (A = , i, ij, ijk, \ldots)
\end{equation}

In these equations, the quantities $Q_A$ are the moments of various order of phase density of kinetic theory of gases [6], $Q_{Ak}$ are the fluxes of fields $Q_A$, 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 $\tilde{Q}_{ijk\ldots t}$ is defined as [6]:

\begin{equation}
(3.2) \quad \tilde{Q}_{ijk\ldots t} = \int mc_i c_j c_k \ldots c_i f dc .
\end{equation}

This paper deals with balance equations for the first 13 moments $Q, Q_i, Q_{ij}, Q_{ij}$
only. Total moments are expressed easily as functions of central moments, in the following way [6],

\begin{align}
q &= \bar{q}, \\
q_i &= \bar{q} v_i = q v_i, \\
q_{ij} &= \bar{q}_{ij} + q v_i v_j, \\
q_{ijk} &= \bar{q}_{ijk} + 3 \bar{q}_{(ij)} v_k + q v_i v_j v_k, \\
q_{ijkl} &= \bar{q}_{ijkl} + 4 \bar{q}_{(ijk)} v_l + 6 \bar{q}_{(ij)} v_k v_l + q v_i v_j v_k v_l,
\end{align}

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

\begin{align}
\dot{\rho} + q \frac{\partial v_k}{\partial x_k} &= 0, \\
\rho \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_{(ij)} \delta_{kj} + \bar{q}_{(ijk)} \right) + 2 p_{j(i)} \frac{\partial v_k}{\partial x_j} &= \bar{P}_{(ik)}, \\
\dot{q}_i + q_i \frac{\partial v_k}{\partial x_k} + q_k \frac{\partial v_i}{\partial x_k} + \bar{q}_{ijk} \frac{\partial v_j}{\partial x_k} + \frac{1}{2} \frac{\partial \bar{q}_{ijk}}{\partial x_k} + \frac{3}{2} q \frac{\partial p_{(ij)} k}{\partial x_k} &= \frac{1}{2} \bar{p}_{ll}.
\end{align}

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

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 \( q_A \) 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 \( q, q_i \) and \( q_{ll} \): 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 \( q \), 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 \( \Lambda_{(ij)} \) 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:

\[
\begin{cases}
\dot{q} + q \frac{\partial v_k}{\partial x_k} = 0, \\
q \dot{v}_i + \frac{\partial p_{ik}}{\partial x_k} = 0, \\
E + E \frac{\partial v_k}{\partial x_k} + \frac{\partial q_k}{\partial x_k} + p_{ik} \frac{\partial v_i}{\partial x_k} = 0, \\
\dot{q}_i + q_i \frac{\partial v_k}{\partial x_k} + q_k \frac{\partial v_i}{\partial x_k} + \tilde{q}_{ijk} \frac{\partial v_j}{\partial x_k} + \frac{1}{2} \frac{\partial \tilde{q}_{ijk}}{\partial x_k} - \frac{3}{2} \tilde{q}_{ij} \frac{\partial p_{ij}}{\partial x_k} = \frac{1}{2} P_{il}.
\end{cases}
\] (3.9)

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

\[
\begin{align*}
p_{ij} &= \frac{2}{3} E \delta_{ij} + a(q, E, q^2) q_i q_j, \\
\tilde{q}_{ijk} &= \frac{2}{5} (q_i \delta_{jk} + q_j \delta_{ki} + q_k \delta_{ij}) + \chi(q, E, q^2) q_i q_j q_k, \\
\tilde{q}_{ijjk} &= \beta(q, E, q^2) \delta_{ik} + \nu(q, E, q^2) q_i q_j q_k,
\end{align*}
\] (3.10, 3.11, 3.12)

where \( a, \chi, \beta \) and \( \nu \) 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:

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

In this inequality, \( h \) and \( \Phi_k \) are objective functions of fundamental fields:

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

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:

\[
\Phi_k = \left[ \tilde{A}_E + \frac{\lambda}{2} \left( \frac{v}{2} - aG \right) q^2 \right] q_k.
\] (3.15)
where we have put $G = \frac{5E + 2aq^2}{3q}$; $\bar{\Lambda}_E$ and $\bar{\lambda}$ 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:

\[
\frac{dh}{dt} + \frac{\partial v_k}{\partial x_k} + \frac{\partial \Phi_k}{\partial x_k} - \bar{\Lambda}_i \left[ \dot{v}_i + \frac{1}{q} \frac{\partial p_{ik}}{\partial x_k} \right] - \bar{\Lambda}_E \left[ \dot{E} + E \frac{\partial v_k}{\partial x_k} + q_k \frac{\partial v_i}{\partial x_k} + p_{ik} \frac{\partial v_i}{\partial x_k} \right] - \\
\bar{\lambda}_i \left[ \dot{q}_i + q_i \frac{\partial v_k}{\partial x_k} + q_k \frac{\partial v_i}{\partial x_k} + \bar{\rho}_{ij} \frac{\partial v_j}{\partial x_k} + \frac{1}{2} \frac{\partial \bar{\rho}_{ijk}}{\partial x_k} - \frac{3}{2q} p_{(ij)} \frac{\partial p_{(jk)}}{\partial x_k} - \frac{1}{2} \bar{P}_{ii} \right] \geq 0.
\]

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

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

\[
\bar{\Lambda}_v = 0, \quad dh = \bar{\Lambda} dq + \bar{\Lambda}_E dE + \bar{\lambda}_i dq_i.
\]

\[
\bar{\Lambda}_E = 0, \quad \bar{\lambda} q^2 = 0, \quad a\bar{\Lambda}_E + \bar{\lambda} \left( \frac{9 + 3q^2}{5} \right) = 0.
\]

\[
d\Phi_k = \bar{\Lambda}_E dq_k + \bar{\lambda}_i \left( \frac{1}{2} d\bar{\rho}_{ijk} - \frac{3}{2q} p_{(ij)} dP_{(jk)} \right).
\]

From (3.19) one can write:

\[
\phi - \bar{\Lambda}_E - \bar{\lambda} q^2 \left[ \frac{v}{2} - aG \right] = 0,
\]

\[
d\phi = \bar{\lambda} \left[ \frac{1}{2} d\beta + \frac{1}{3} q^2 dv + \frac{1}{6} \left( \frac{v}{2} - aG \right) dE - \frac{1}{6} G(4dE + 4q^2 da) \right].
\]

Using (3.14) and (3.20), equation (3.15) is obtained.
Remark 3.1. – Denoting with \( \frac{1}{T_{th}} \) the coefficient linking \( \Phi_k \) and \( q_k \), one obtains:

\[
T_{th} = \frac{1}{\Lambda_E + \lambda q^2 \left[ \frac{\nu}{2} - aG \right]}
\]

while \( \theta = \frac{1}{\Lambda_E} \).

3.1. Approximate constitutive relations.

In this subsection only processes near equilibrium will be considered. Denote with \( \hat{r} \) any of the 9 quantities \( h, \phi, \alpha, \beta, \nu, \chi, \Lambda, \Lambda_E \) and \( \lambda \), and put:

\[
\hat{r} = \hat{r}_0(q, E) + \hat{r}_1(q, E)q^2 + \mathcal{O}(q^4).
\]

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

\[
\begin{align*}
2h_1 - \lambda_0 &= 0, \\
h_0 - \nu A_0 - \frac{5}{3} E A'_E &= 0, \\
\phi_0 - \bar{A}'_E &= 0, \\
4h_2 - \lambda_1 &= 0, \\
a_0\bar{A}'_E + \frac{9}{5} \lambda_0 &= 0, \\
h_1 - \nu A_1 - \frac{5}{3} E A''_E - 2\lambda_0 &= 0, \\
2\phi_1 - \lambda_0 \left[ \beta_1 + \frac{1}{6} \nu_0 - \frac{5E}{9Q} a_0 \right] &= 0, \\
5\phi_1 - 3 \bar{A}_E - \lambda_0 \left( \beta_1 + \frac{5}{3} \nu_0 - \frac{50E}{9Q} a_0 \right) &= 0,
\end{align*}
\]

and the following differential relations:

\[
\begin{align*}
dh_0 &= \bar{A}_0 dq + \bar{A}_E^0 dE, \\
d\phi_0 &= \lambda_0 \left[ \frac{1}{2} d\beta_0 - \frac{10E}{9Q} dE \right], \\
dh_1 &= \bar{A}_1 dq + \bar{A}_E^{(1)} dE,
\end{align*}
\]
Equation (3.1.10) can be written:

\[
(3.1.14) \quad d \left( \frac{h_0}{Q} \right) = \tilde{A}_E^0 \left[ d \left( \frac{E}{Q} \right) - \frac{p}{Q^2} dQ \right].
\]

Denoting with \( \eta_0 = h_0/Q \) and \( \varepsilon = E/Q \) the equilibrium specific entropy and the specific internal energy respectively, and identifying \( \tilde{A}_E^0 \) with the inverse of absolute equilibrium temperature \( T \), the Gibbs equation of thermostatic is obtained:

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

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

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

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

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

which yields the following integrability conditions:

\[
(3.1.18) \quad \frac{1}{2} \frac{\partial \beta_0}{\partial Q} - \frac{5}{3} \frac{\varepsilon}{Q} \frac{\partial p}{\partial Q} = 0, \quad \frac{1}{2} \frac{\partial \beta_0}{\partial T} - \frac{5}{3} \frac{\varepsilon}{T} \frac{\partial p}{\partial T} = - \frac{1}{T^2 \lambda_0}.
\]

Putting:

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

one can write:

\[
(3.1.20) \quad \tilde{\lambda}_0 = - \frac{1}{T^2 \zeta}, \quad h_1 = - \frac{1}{2 T^2 \zeta},
\]

\[
(3.1.21) \quad a_0 = - \frac{9 \lambda_0}{5 A_E^0} = \frac{9}{5 T \zeta}, \quad \phi_1 = - \frac{1}{4 T^2 \zeta} \left( 2 \beta_1 + \frac{1}{3} \nu_0 - \frac{3 p}{\varrho T \zeta} \right).
\]
Substituting this latter quantity in (3.14) one gets the following expression of entropy flux approximate to third order in $q_i$,

\begin{equation}
(3.1.22) \quad \Phi_k = \left( \frac{1}{T} - \frac{1}{4T^2 \zeta} \left( 2\beta_1 + \frac{1}{3} v_0 - \frac{3p}{qT\zeta} \right) q^2 \right) q_k + \mathcal{O}(q^4).
\end{equation}

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

\begin{equation}
(3.1.23) \quad T_{th} - \theta = -\lambda_0 T \left( \frac{v_0}{2} - \frac{5a_0}{3Q} E \right) q^2 + \mathcal{O}(q^4),
\end{equation}

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

REFERENCES


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