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Thermodynamics of non-local materials: extra fluxes and internal powers

Abstract The most usual formulation of the Laws of Thermodynamics turns out to be suitable for local or simple materials, while for non-local systems there are two different ways: either modify this usual formulation by introducing suitable extra fluxes or express the Laws of Thermodynamics in terms of internal powers directly, as we propose in this paper.

The first choice is subject to the criticism that the vector fluxes must be introduced a posteriori in order to obtain the compatibility with the Laws of Thermodynamics. On the contrary, the formulation in terms of internal powers is more general, because it is a priori defined on the basis of the constitutive equations. Besides it allows to highlight, without ambiguity, the contribution of the internal powers in the variation of the thermodynamic potentials.

Finally, in this paper, we consider some examples of non-local materials and derive the proper expressions of their internal powers from the power balance laws.

Keywords Thermodynamics · Non-local materials · Constitutive theories

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1 Introduction

The modern approach to the thermodynamics of continuous systems, known as Rational Thermodynamics, traces back to the works of Coleman, Gurtin, Noll and Truesdell [6], [18], [30], [33]. It’s our opinion that this important new approach in the study of thermodynamic phenomena has achieved its formal stage in the papers of Noll [31] and Coleman and Owen [7]. As it is well known, this innovative point of view distinguishes the field equations, which hold for all systems, from the constitutive equations, which characterize the materials. Moreover, according to this school, restrictions on the constitutive equations can be obtained from the Principles of Thermodynamics.

In most of the works of the previously cited authors only simple materials are considered. These systems are defined by Truesdell [33, pag.35] as those materials for which everything there is to know can be found out by performing experiments on homogeneous motions of a body of those materials, from whatever state they happen to find in it. In the same book, Truesdell gives also a formal definition of simple materials, in presence of purely mechanical and isothermal processes, through the constitutive equation $T(x,t) = \hat{T}(F^t(x,\cdot);x)$ which links the stress tensor $T$ to the history up to time $t$ of the strain gradient $F$, at any point $x$ of the body $B$.

A more rigorous and general definition of simple material can be found in [31] and [7]. These materials are always characterized by the fact that the First Law of Thermodynamics is given by

$$\rho \frac{d}{dt} e = T \cdot L - \nabla \cdot q + \rho r,$$

(1.1)
where $\rho$ is the mass density, $e$ the internal energy, $\mathbf{L}$ the velocity gradient, $\mathbf{q}$ the heat flux and $r$ the heat supply, while the Second Law of Thermodynamics is formulated through the Clausius-Duhem inequality

$$\rho \frac{d}{dt} \eta \geq -\nabla \cdot \left( \frac{\mathbf{q}}{\theta} \right) + \rho \frac{r}{\theta},$$

(1.2)

$\eta$ being the specific entropy density and $\theta$ the absolute temperature.

The expressions (1.1) and (1.2) of the First and Second Law of Thermodynamics cannot be applied to those systems, called non-local or non-simple materials, for which the constitutive equations for $\mathbf{T}$ and $\mathbf{q}$ depend on the gradients of order higher than the first of the thermo-kinetic variables ($\mathbf{F}, \theta$).

In order to understand how it is possible to give a formulation of the First Law of Thermodynamics for a wider class of materials, we consider the heat balance equation

$$\rho h = -\nabla \cdot \mathbf{q} + \rho r,$$

(1.3)

where $h$ is the rate at which the heat is absorbed per unit mass. By comparing (1.3) with (1.1), the First Law of Thermodynamics for simple materials can be rewritten as follows

$$\rho \frac{d}{dt} e = \mathbf{T} \cdot \mathbf{L} + \rho h.$$

(1.4)

Moreover, following many classical texts of Thermodynamics (Truesdell [35], Gurtin [17], Germain [15, 16], etc.), we introduce the internal mechanical power $P^i_m$ and the internal heat power $P^i_h = \rho h$. Then the balance equation for the energy (1.4) assumes the classical form

$$\rho \frac{d}{dt} e = P^i_m + P^i_h,$$

(1.5)

which is more general and can also be applied to non-simple materials. Obviously it coincides with (1.3) when

$$P^i_m = \mathbf{T} \cdot \mathbf{L},$$

(1.6)

but this choice, which is surely correct for simple materials, cannot be assumed in general. For this reason Dunn and Serrin [8] suggested to change the formulation (1.1) of the First Law of Thermodynamics with the new expression

$$\rho \frac{d}{dt} e = \mathbf{T} \cdot \mathbf{L} - \nabla \cdot \mathbf{N} - \nabla \cdot \mathbf{q} + \rho r,$$

(1.7)

where $\mathbf{N}$ is called interstitial work flux. Expression (1.7) has been actually introduced by the authors for some non-simple materials including the elastic materials of grade three and the subclass of materials of Korteweg type, but its framework is more general (13-27).

In this paper we start from the statement that the representations (1.1) or (1.3) of the First Law of Thermodynamics cannot have universal character and propose the more general classical formulation (1.5), where the internal mechanical power $P^i_m$ will assume different expressions depending on the materials under study.

It is also interesting to observe that a comparison between Dunn and Serrin’s formulation (1.7) and the classical one (1.5) gives

$$P^i_m = \mathbf{T} \cdot \mathbf{L} - \nabla \cdot \mathbf{N},$$

(1.8)

which turns out to be an indirect way to define $P^i_m$. Let us consider, as an example, the constitutive equation for the stress tensor of a second grade material, i.e.

$$\mathbf{T} = \mathbf{T}_2 + \nabla \cdot \mathbf{T}_3,$$

where $\mathbf{T}_2$ and $\mathbf{T}_3$ are respectively second and third order tensors. The internal mechanical power is given by (3-13-16)

$$P^i_m = \mathbf{T}_2 \cdot \nabla \mathbf{v} - \mathbf{T}_3 \cdot \nabla(\nabla \mathbf{v}).$$

(1.9)

Since

$$\mathbf{T}_3 \cdot \nabla(\nabla \mathbf{v}) = \nabla \cdot (\mathbf{T}_3 \nabla \mathbf{v}) - (\nabla \cdot \mathbf{T}_3) \cdot \nabla \mathbf{v},$$

Only recently it has been observed that expression (1.7) and the introduction of the extra-flux $\mathbf{N}$ in the First Law of Thermodynamics had been already proposed in 1982 by T. Manacorda [25], see also [26].
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expression (1.8) turns out to be equivalent to (1.9) introducing the vector
\[ N = T_3 \nabla \nu. \]

Nevertheless, we prefer the representation of the internal mechanical power (1.9), since it is in agreement with the expression of the internal power as a differential form and since (1.8) results a "hybrid" form because it contains a term of ambiguous differential type, \( T \cdot L \), and a flux term.

Similar arguments can be applied to many non-local mechanical materials, to the study of the phase transitions of superconductors and superfluids, to the transition of a binary mixture satisfying the Cahn-Hilliard equations and, in electromagnetism, to dielectric media with quadrupoles.

In literature some authors maintain the expression (1.1) for the First Law of Thermodynamics and, in presence of the above non-simple materials, modify the Clausius-Duhem inequality (1.2). They consider, as suggested in 1967 by Müller [29], the following inequality
\[ \rho \frac{d}{dt} \eta \geq -\nabla \cdot \Phi + \rho \frac{r}{\theta}, \tag{1.10} \]

where the vector \( \Phi \), still called entropy flux, can be defined by
\[ \Phi = \Phi' + \frac{q}{\theta}. \tag{1.11} \]

\( \Phi' \) being the *entropy extra-flux*.

This approach is useful only in presence of non-local effects on the heat flux. Instead it is not fruitful in the study of materials with constitutive equations describing non-local behaviors in mechanics, electromagnetism, chemistry, etc.. For these materials the Second Law assumes the classical form (1.2), while we need to provide a suitable expression for the (mechanical, chemical, electromagnetic, etc.) internal powers to use in the First Law.

On the other hand, some thermal effects are well described by non-local models for which the Clausius-Duhem inequality (1.2) must be substituted by (1.10). An example is the Guyer-Krumhansl equation [20,21],
\[ \frac{d}{dt} q + \frac{q}{\tau} = -\kappa(\theta) \nabla \theta + \alpha(\nabla \cdot \nabla q + 2 \nabla \cdot q), \tag{1.12} \]

which has been derived by solving the linearized Boltzmann equation of phonon gas hydrodynamics. Here \( \tau, \kappa \) and \( \alpha \) are suitable constitutive coefficients and this model, as proved in [4], satisfies the inequality (1.10) by choosing
\[ \Phi' = \frac{\alpha}{\kappa} (\nabla q) q + 2 q \nabla \cdot q. \]

The presence of the extra-fluxes \( N \) in (1.8) and \( \Phi' \) in (1.10)-(1.11) opens to the criticism of a formulation of the Principles of Thermodynamics which turns out to be not universal, since these vectors must be defined a posteriori.

As we have already observed, a general formulation for the First Law of Thermodynamics is given by (1.5), where the internal power densities \( P_{im} \) and \( P_{ih} \) are a priori defined on the basis of the constitutive equations. In order to get a similar general expression for the Second Law of Thermodynamics, we introduce the entropy balance equation
\[ \rho \frac{h}{\theta} = \frac{1}{\theta} \nabla \cdot q + \rho \frac{r}{\theta}, \tag{1.13} \]

which can be derived multiplying equation (1.3) by the coldness \( \theta^{-1} \).

This equation distinguishes between the contributions of the internal and external actions because (1.13) can be rewritten as
\[ \rho \frac{h}{\theta} + \frac{1}{\theta^2} q \cdot \nabla \theta = -\nabla \cdot \left( \frac{q}{\theta} \right) + \rho \frac{r}{\theta}. \tag{1.14} \]

For simple materials in the heat flux (i.e. for materials with a local constitutive equation for the heat flux), we define *internal entropy action* the left-hand side of (1.14), which is a differential form, and *external entropy action* the right-hand side of (1.14), i.e.
\[ \mathcal{A}_{en} = \rho \frac{h}{\theta} + \frac{1}{\theta^2} q \cdot \nabla \theta, \quad \mathcal{A}_{en} = -\nabla \cdot \left( \frac{q}{\theta} \right) + \rho \frac{r}{\theta}. \tag{1.15} \]
Therefore, thanks to (1.14), the usual Clausius-Duhem inequality (1.2) assumes the equivalent form
\[ \rho \frac{d}{dt} \eta \geq \frac{h}{\theta} + \frac{1}{\theta^2} q \cdot \nabla \theta \] (1.16)
or, by virtue of (1.15), it can be expressed only by means of the internal entropy action as follows
\[ \rho \frac{d}{dt} \eta \geq \mathcal{A}_{en}^i. \] (1.17)

We observe that the expression (1.16) holds only for simple materials in the heat flux, while the relation (1.17) is consistent also with the modified Clausius-Duhem inequality (1.10) when the internal entropy action is given by
\[ \mathcal{A}_{en}^i = \frac{h}{\theta} + \frac{1}{\theta^2} q \cdot \nabla \theta - \nabla \cdot \Phi'. \] (1.18)

It is therefore clear that it is necessary to give a proper definition of internal and external entropy action. In fact, if for example we consider a heat conductor of Guyer-Krumhansl type (1.12) with \( \kappa(\theta) = \frac{c}{\theta^2} \), the entropy balance equation becomes
\[ \rho \eta \frac{h}{\theta} - \frac{d}{dt} \left( \frac{q^2}{2c} \right) - \frac{1}{c r} q^2 - \alpha \frac{c}{c} \left( |\nabla q|^2 + 2 |\nabla \cdot q|^2 \right) = -\nabla \cdot \left[ \frac{q}{\theta} + \frac{\alpha}{c} \left( (\nabla q) q + 2q \nabla \cdot q \right) \right] + \rho \frac{r}{\theta}. \]

Since
\[ q \cdot (\nabla \cdot \nabla q + 2 \nabla \cdot q) = \nabla \cdot \left[ (|\nabla q|^2 + 2 |\nabla \cdot q|^2 \right] - |\nabla q|^2 - 2 |\nabla \cdot q|^2, \]
we obtain
\[ \rho \frac{h}{\theta} - \frac{d}{dt} \left( \frac{q^2}{2c} \right) - \frac{1}{c r} q^2 - \alpha \frac{c}{c} \left( |\nabla q|^2 + 2 |\nabla \cdot q|^2 \right) = -\nabla \cdot \left[ \frac{q}{\theta} + \frac{\alpha}{c} \left( (\nabla q) q + 2q \nabla \cdot q \right) \right] + \rho \frac{r}{\theta}. \]

It follows that, for such material, the internal entropy action is defined by
\[ \mathcal{A}_{en}^i = \rho \frac{h}{\theta} - \frac{d}{dt} \left( \frac{q^2}{2c} \right) - \frac{1}{c r} q^2 - \alpha \frac{c}{c} \left( |\nabla q|^2 + 2 |\nabla \cdot q|^2 \right), \]
while the external entropy action is given by
\[ \mathcal{A}_{en}^e = \rho \frac{r}{\theta} - \nabla \cdot \left[ \frac{q}{\theta} + \frac{\alpha}{c} \left( (\nabla q) q + 2q \nabla \cdot q \right) \right]. \] (1.19)

Finally, in this paper, we suggest to describe the evolution of a thermodynamic system through the virtual mechanical power and entropy action. To this end, it is important to introduce the domain \( \Omega \subset \mathbb{R}^3 \) on which are defined the fields and the processes of the virtual velocity \( \tilde{v} \) and of the virtual temperature \( \tilde{\theta} \). By denoting the internal and external virtual mechanical powers respectively with \( \tilde{\mathcal{P}}_m^i, \tilde{\mathcal{P}}_m^e \) and the internal and external virtual entropy actions with \( \tilde{\mathcal{A}}_{en}^i, \tilde{\mathcal{A}}_{en}^e \), we are now able to write the balance equation for the virtual mechanical power
\[ \int_{\Omega} \rho \frac{d}{dt} \tilde{v} \cdot \tilde{v} \, dx + \int_{\Omega} \tilde{\mathcal{P}}_m^i \, dx = \int_{\Omega} \tilde{\mathcal{P}}_m^e \, dx \]
and the balance equation for the virtual entropy action
\[ \int_{\Omega} \tilde{\mathcal{A}}_{en}^i \, dx = \int_{\Omega} \tilde{\mathcal{A}}_{en}^e \, dx. \]

In presence of simple materials, the previous equations become
\[ \int_{\Omega} \rho \frac{d}{dt} \tilde{v} \cdot \tilde{v} \, dx + \int_{\Omega} \tilde{T} \cdot \nabla \tilde{v} \, dx = \int_{\Omega} \left[ \nabla \cdot (\tilde{T} \tilde{v}) + \rho \tilde{f} \cdot \tilde{v} \right] \, dx, \]
\[ \int_{\Omega} \left[ \rho \frac{h}{\tilde{\theta}} - \frac{1}{\tilde{\theta}^2} q \cdot \nabla \tilde{\theta} \right] \, dx = \int_{\Omega} \left[ -\nabla \cdot \left( \frac{q}{\tilde{\theta}} \right) + \rho \frac{r}{\tilde{\theta}} \right] \, dx, \]
where \( \tilde{f} \) denotes the external forces and the symmetry the the stress tensor \( \tilde{T} \) is assumed.
2 Definition of thermo-mechanical material as dynamic system

The thermo-mechanical properties of a material are based on the notion of state and process. Here we provide these notions following Noll [31] and Coleman and Owen [7] (see also [11]).

We consider a body occupying the placement \( \mathcal{B} \). For any material point \( x \in \mathcal{B} \), a thermo-mechanical process \( P \) in \( X \) of duration \( d_P > 0 \), is a piecewise continuous function on \([0, d_P)\) with values in \( E \), open and connected subset of a vectorial space.

The notation \( P_{[t_1, t_2]} \) denotes the restriction of \( P \) to \( [t_1, t_2) \subset [0, d_P) \). In particular, we denote by \( P_t \) the restriction of \( P \) to the interval \([0, t) \leq d_P \). Let \( P_1 \) and \( P_2 \) be two processes of duration \( d_{P_1} \) and \( d_{P_2} \), the composition \( P_1 \star P_2 \) of \( P_2 \) with \( P_1 \) is defined as

\[
P_1 \star P_2 = \begin{cases} P_1(t), & t \in [0, d_{P_1}) \\ P_2(t - d_{P_1}), & t \in [d_{P_1}, d_{P_1} + d_{P_2}) \end{cases}
\]

We can therefore give the following definition of thermo-mechanical material as dynamic system.

**Definition 2.1** Let \( \mathcal{B}_t \) the placement occupied by the body at time \( t \). A thermo-mechanical system, at any \( t \) and \( x \in \mathcal{B}_t \), is a set \( \{\mathcal{H}, \mathcal{V}_t, \Sigma, \hat{\Sigma}, \mathcal{U}\} \) such that

1. \( \mathcal{H} \) is the space of the thermo-mechanical processes \( P \) satisfying the following properties:
   i) if \( P \in \mathcal{H} \), then \( P_{[t_1, t_2]} \in \mathcal{H} \) for every \( [t_1, t_2) \subset [0, d_P) \),
   ii) if \( P_1, P_2 \in \mathcal{H} \), then \( P_1 \star P_2 \in \mathcal{H} \),
2. \( \mathcal{V}_t \) is the space of the virtual thermo-mechanical processes \( \hat{\mathcal{V}}_t \), i.e. the space of the processes that may be specified independently of the actual evolution of the system at some arbitrarily chosen but fixed time \( t \),
3. \( \hat{\Sigma} \) is an abstract set, called state space, whose elements \( \sigma \) are called states,
4. \( \hat{\chi} : \hat{\Sigma} \times \mathcal{H} \rightarrow \Sigma \) is a map, called state transition function which assigns, to each state \( \sigma \) and process \( P \), the state at the end of the process and satisfies the following relation

\[
\hat{\chi}(\sigma, P_1 \star P_2) = \hat{\chi}(\chi(\sigma, P_1), P_2) , \quad \sigma \in \hat{\Sigma}, P_1, P_2 \in \mathcal{H},
\]

5. for any state \( \sigma \), process \( P \) of duration \( d_P \), time \( t \in [0, d_P) \) and virtual process \( \hat{\mathcal{V}}_t \), it is defined the response function at time \( t \)

\[
\hat{\mathcal{U}}_t : \hat{\Sigma} \times \mathcal{E} \times \hat{\mathcal{V}}_t \rightarrow \mathbb{R} \times \mathbb{R}
\]

which assigns the internal virtual mechanical power \( \hat{\mathcal{P}}_m^i \) and the internal virtual entropy action \( \hat{\mathcal{A}}_{en}^i \), namely

\[
\hat{\mathcal{U}}(t) = \hat{\mathcal{U}}_t(\sigma_t, \mathcal{P}(t), \hat{\mathcal{V}}_t) = (\hat{\mathcal{P}}_m^i(\sigma_t, \mathcal{A}_{en}^i)) t \in [0, d_P),
\]

where \( \sigma_t = \hat{\chi}(\sigma, P_t) \).

**Remark 2.1** Because of the linear dependence of the virtual power and action on the virtual processes, the function \( \hat{\mathcal{U}}(t) \) is linear with respect to \( \hat{\mathcal{V}}_t \).

**Remark 2.2** The knowledge of \( \hat{\mathcal{P}}_m^i \) and \( \hat{\mathcal{A}}_{en}^i \) allows to define the internal mechanical power \( \mathcal{P}_m^i \) and the internal entropy action \( \mathcal{A}_{en}^i \). Moreover, if we restrict \( \hat{\mathcal{A}}_{en}^i \) to spatial homogeneous thermal processes, we can also define \( h \) and the heat flux power \( \mathcal{P}_q = \mathcal{A}_{en}^i - \rho \hat{\mathcal{V}}_t h \).

3 Thermodynamic Laws

In order to introduce the Thermodynamic Laws, following [7], we introduce the notion of cycle.

**Definition 3.1** A pair \((\sigma, P) \in \Sigma \times \mathcal{H}\) is called a cycle if \( \hat{\chi}(\sigma, P) = \sigma \).

**First Law of Thermodynamics.** In any cycle \((\sigma, P)\) the sum of the rate at which the heat is absorbed by the body and the power of the internal forces vanishes, i.e.

\[
\int_0^{d_P} \left\{ \rho h(\sigma_t, \mathcal{P}(t)) + \mathcal{P}_m^i(\sigma_t, \mathcal{P}(t)) \right\} dt = 0.
\]

A consequence of the First Law of Thermodynamics is the following theorem
Theorem 3.1 The First Law of Thermodynamics implies the existence of a unique (up to an additive constant) continuous function \( e : \Sigma \rightarrow \mathbb{R} \), called internal energy, such that, for any pair of states \( \sigma_1, \sigma_2 \) and process \( P \) with \( \hat{\chi}(\sigma_1, P) = \sigma_2 \), we have

\[
\rho e(\sigma_2) - \rho e(\sigma_1) = \int_0^{d_P} \left\{ \rho h(\sigma_1, P(t)) + P_m^{\frac{1}{t}}(\sigma_t, P(t)) \right\} dt.
\]

Moreover, under suitable hypotheses of regularity on the constitutive functionals,

\[
\rho \frac{d}{dt} e(\sigma_t) = \rho h(\sigma_t, P(t)) + P_m^{\frac{1}{t}}(\sigma_t, P(t)) \tag{3.1}
\]

for any instant \( t \) of continuity of the right-hand term in (3.1).

Second Law of Thermodynamics. In any cycle \((\sigma, P)\) the internal entropy action is non-positive, i.e.

\[
\oint_0^{d_P} A_{en}^i(\sigma_t, P(t)) dt \leq 0.
\]

As a consequence of the Second Law of Thermodynamics we get the following theorem

Theorem 3.2 The Second Law of Thermodynamics implies the existence of at least one upper semicontinuous function \( \eta : \Sigma \rightarrow \mathbb{R} \), called entropy, such that, for any pair of states \( \sigma_1, \sigma_2 \) and process \( P \) with \( \hat{\chi}(\sigma_1, P) = \sigma_2 \), we have

\[
\rho \eta(\sigma_2) - \rho \eta(\sigma_1) \geq \int_0^{d_P} A_{en}^i(\sigma_t, P(t)) dt.
\]

Moreover, under suitable hypotheses of regularity on the constitutive functionals,

\[
\rho \frac{d}{dt} \eta(\sigma_t) \geq A_{en}^i(\sigma_t, P(t)) \tag{3.2}
\]

for any instant \( t \) of continuity of the right-hand term in (3.2).

When only isothermal processes are involved, the two Laws of Thermodynamics are replaced by the Dissipation Principle of mechanical work.

Dissipation Principle. In any cycle \((\sigma, P)\) the internal mechanical power is non-negative, i.e.

\[
\oint_0^{d_P} P_m^{\frac{1}{t}}(\sigma_t, P(t)) dt \geq 0.
\]

A consequence of the Dissipation Principle is the following theorem

Theorem 3.3 The Dissipation Principle implies the existence of at least one lower semicontinuous function \( \psi : \Sigma \rightarrow \mathbb{R} \), called free energy, such that, for any pair of states \( \sigma_1, \sigma_2 \) and process \( P \) with \( \hat{\chi}(\sigma_1, P) = \sigma_2 \), we have

\[
\rho \psi(\sigma_2) - \rho \psi(\sigma_1) \leq \int_0^{d_P} P_m^{\frac{1}{t}}(\sigma_t, P(t)) dt.
\]

Moreover, under suitable hypotheses of regularity on the constitutive functionals,

\[
\rho \frac{d}{dt} \psi(\sigma_t) \leq P_m^{\frac{1}{t}}(\sigma_t, P(t)) \tag{3.3}
\]

for any instant \( t \) of continuity of the right-hand term in (3.3).
4 Virtual powers and thermo-mechanical materials

For a thermo-mechanical system, we define the field of the generalized virtual motions at time $t$ as the pair

$$\vec{v}_t(\cdot) = \left( \vec{v}_t(\cdot), \frac{1}{\theta_t(\cdot)} \right),$$

where $\vec{v}_t(\cdot)$ and $\frac{1}{\theta_t(\cdot)}$ denote respectively the vector field of the virtual velocities and the virtual coldness on $B_t$.

The virtual powers of the internal forces at any $x$ in $B_t$ are taken as linear forms in the gradients of the virtual motions $\vec{v}_t$ evaluated at $x$. For a large class of materials we can represent the internal virtual mechanical power as

$$\tilde{P}_m^i(t,x) = \sum_{i \geq 1} T_{i+1}(t,x) \cdot \nabla^{(i)} \vec{v}_t(x)$$

where $\nabla^{(n)}$ denotes the gradient of order $n$ and $T_k$ is a tensor of order $k$. Moreover, the internal virtual entropy action is defined by

$$\tilde{A}_{en}^i(t,x) = \frac{1}{\theta_t(x)} \varrho(t,x) h(t,x) - \sum_{i \geq 1} q_i(t,x) \cdot \nabla^{(i)} \left[ \frac{1}{\theta_t(x)} \right]$$

where $q_i$ is a tensor of order $i$. Finally, the virtual mechanical power and entropy action of the external and contact forces are respectively given by

$$\tilde{P}_m^e(t,x) = \nabla \cdot \left[ \sum_{i \geq 1} T_{i+1}(t,x) \nabla^{(i-1)} \vec{v}_t(x) \right] + \rho(t,x) f(t,x) \cdot \vec{v}_t(x),$$

$$\tilde{A}_{en}^e(t,x) = -\nabla \cdot \left( \sum_{i \geq 1} q_i(t,x) \nabla^{(i-1)} \left[ \frac{1}{\theta_t(x)} \right] \right) + \rho(t,x) r(t,x) \frac{1}{\theta_t(x)}.$$  

The principle of virtual power is the requirement that the external and internal virtual powers and entropy actions be balanced, i.e.

$$\varrho(t,x) \frac{d}{dt} \vec{v}(t,x) \cdot \vec{v}_t(x) + \tilde{P}_m^i(t,x) + \tilde{P}_m^e(t,x) = \tilde{A}_{en}^i(t,x), \quad \tilde{A}_{en}^e(t,x) = \tilde{A}_{en}^e(t,x)$$

for any generalized virtual motion.

From now on, whenever no ambiguity arises, the dependence on $x$ and $t$ will be understood and not written.

**Definition 4.1** A thermo-mechanical material is called a *simple material* if

$$T_{i+1} = 0, \quad q_i = 0, \quad i \geq 2$$

for any time $t$ and $x \in B_t$. Otherwise it is called *non-simple material*.

**Remark 4.1** From the previous definition, it follows that, in presence of a simple material, becomes

$$\tilde{P}_m^i(\sigma, P, \gamma_t) = T_2(\sigma, P) \cdot \nabla \vec{v}_t,$$

$$\tilde{A}_{en}^i(\sigma, P, \gamma_t) = \rho \varrho(\sigma, P) \frac{1}{\theta_t} - q_1(\sigma, P) \cdot \nabla \left[ \frac{1}{\theta_t} \right],$$

where $T_2$ is the classical Cauchy stress tensor and $q_1$ is the Fourier heat flux vector. It should be noticed that the arbitrariness of the virtual process yields that the triplet $(T_2, h, q_1)$ is uniquely determined when the internal virtual power and entropy action are known. This is in agreement with the well known rational thermodynamic theories ([5], [6], [7], [30], [31], [33], [34], [35]).
By using the classical notations \((T, h, q)\) instead of \((T, h, q_1)\) and \((L, \dot{\theta}, g)\) instead of \((\nabla \nu, \dot{\nu}, \nabla \theta)\) (where the dot denotes the time derivative), the relations (3.1) and (3.2) become
\[
\frac{d}{dt} \sigma_t = h(\sigma_t, P(t)) + \frac{1}{\rho} T(\sigma_t, P(t)) \cdot L(t), \tag{4.4}
\]
\[
\frac{d}{dt} \eta(\sigma_t) \geq \frac{h(\sigma_t, P(t))}{\theta(t)} + \frac{1}{\rho \theta(t)} q(\sigma_t, P(t)) \cdot g(t). \tag{4.5}
\]
Moreover, introducing the free energy potential
\[
\psi = e - \theta \eta, \tag{4.6}
\]
(4.4) and (4.5) yield
\[
\frac{d}{dt} \psi(\sigma_t) \leq \frac{1}{\rho} T(\sigma_t, P(t)) \cdot L(t) - \frac{1}{\rho \theta(t)} q(\sigma_t, P(t)) \cdot g(t) - \dot{\theta}(t) \eta(\sigma_t).
\]
In the context of the theory of simple materials it is possible to obtain mathematical models well describing the thermo-mechanical behavior of several materials. Here we recall the most elementary examples.

- **Classical Thermoelastic Systems**
  The state of these materials is given by the deformation gradient \(F\) and the absolute temperature \(\theta\), i.e. \(\sigma = (F, \theta)\), and the constitutive equations are:
  \[
  T = T(\sigma), \quad h = A(\sigma) \cdot L + B(\sigma) \dot{\theta}, \quad q = K(\sigma) g.
  \]

- **Newtonian Viscous Fluids**
  The state of these materials is given by the mass density \(\varrho\) and the absolute temperature \(\theta\), i.e. \(\sigma = (\varrho, \theta)\), and the constitutive equations are:
  \[
  T = [-p(\sigma) + \lambda(\sigma) \text{tr} D] I + 2\mu(\sigma) D, \quad h = A_1(\sigma) \dot{\theta} + B_1(\sigma) \dot{\theta}, \quad q = K(\sigma) g,
  \]
  where \(D = \text{sym}\{L\}\).

- **Materials with Fading Memory**
  The state of these materials is given by the histories of the deformation gradient \(F^t\) and the absolute temperature \(\theta^t\), i.e. \(\sigma = (F^t, \theta^t)\), and the constitutive equations are:
  \[
  T = T^t(\sigma), \quad h = A^t(\sigma) \cdot L + B^t(\sigma) \dot{\theta}, \quad q = K^t(\sigma) g.
  \]

- **Materials with internal variables**
  The state of these materials is given by the deformation gradient \(F\), the absolute temperature \(\theta\) and the internal variables \(\alpha \in \mathbb{R}^n\), i.e. \(\sigma = (F, \theta, \alpha)\), and the constitutive equations are:
  \[
  T = T^*(\sigma), \quad h = A^*(\sigma) \cdot L + B^*(\sigma) \dot{\theta}, \quad q = K^*(\sigma) g.
  \]

## 5 Non-Simple Materials

As already observed in the Introduction, a significant difference between simple and non-simple materials is pointed out when the mechanic power and entropy action are defined. For simple materials, the internal mechanical power \(P_m^i\) is always expressed by (1.6) and, therefore, the First Law assumes the form (1.1) or (1.4), while the internal entropy action \(A_m^e\) has always the form (1.13) and the Second Law is given by the Clausius-Duhem inequality (1.2).

For more general materials there are two ways: either (1.1) and (1.2) must be modified introducing suitable extra fluxes, as proposed by Dunn and Serrin \cite{8} and Müller \cite{29}, or the expressions of the internal mechanical powers and of the internal entropy actions \(P_m^i\) and \(A_m^e\) must be properly derived from the power balance laws.

If we choose the first option, the First and Second Law of Thermodynamics are respectively expressed by (1.7) and (1.10). It should be noted that the internal powers and actions defined in (1.8) and (1.18) are not given by a differential form, but by a hybrid representation containing also external fluxes. In any case, we prefer the second option also because it allows us to highlight, without ambiguity, the contribution of the internal mechanical power and entropy action in the variation of the thermodynamic potentials.
5.1 Second grade materials

In this subsection we limit our attention to second grade materials.

**Definition 5.1** A thermo-mechanical material is called a *second grade material* if

\[ T_{i+1} = 0, \quad q_i = 0, \quad i \geq 3 \]

for any time \( t \) and \( x \in B_t \).

In the sequel we will show how through our theory it is possible to obtain a framework in agreement with the thermodynamic principles.

### 5.1.1 First Law of Thermodynamics

For second grade materials, taking into account Definition 5.1, (4.1) becomes

\[ \tilde{P}_{in}^m(\sigma, P, \tilde{\nu}_t) = T_2(\sigma, P) \cdot \nabla T + T_3(\sigma, P) \cdot \nabla^{(2)} \tilde{\nu}_t, \]

This expression fully agrees with the wide literature on these materials. Among all the papers, we recall the one by Fried and Gurtin [13]. Here the authors, in accordance with [16], introduce a general virtual power principle by asserting that the internal power has the form

\[ W_{int} = \int_\Omega \left( T_2 \nabla v + T_3 \nabla^{(2)} v \right) dx, \quad (5.1) \]

where \( T_2 \) and \( T_3 \) are respectively second and third-order tensors. Moreover they observe that it is reasonable to modify also the classical kinetic energy and introduce a generalized kinetic energy

\[ K^* = \frac{1}{2} (\rho v^2 + \beta |\nabla v|^2) \]

to take into account its dependence on the gradient of velocity.

This last observation allows us to study, within this theory, also the Kirchhoff thermoelastic plate. Following [10], [22], [23], the constitutive equation for the stress tensor is

\[ T = -a \nabla (\triangle u) + c \nabla \theta + T_K \quad (5.2) \]

where \( \triangle \) denotes the Laplace operator, \( u \) is the vertical displacement, \( T_K = b \nabla \tilde{u} \) is called kinetic stress and \( a, b \) and \( c \) are suitable material constants.

Multiplying the equation of motion

\[ \rho \ddot{u} = \nabla \cdot T + \rho f \]

by \( \dot{u} \), we obtain

\[ \frac{d}{dt} \left( \frac{1}{2} \rho \dot{u}^2 \right) = \nabla \cdot (T \dot{u}) - T \cdot \nabla \dot{u} + \rho f \dot{u} \quad (5.3) \]

and making use of the constitutive relation (5.2) the balance equation of the mechanical powers assumes the following form

\[ \frac{1}{2} \frac{d}{dt} \left[ \rho \ddot{u}^2 + a (\triangle u)^2 + b (\nabla \dot{u})^2 \right] = \nabla \cdot \left\{ [-a \nabla (\triangle u) + b \nabla \dot{u} + c \nabla \theta] \dot{u} + (a \triangle u - \theta) \nabla \dot{u} \right\} + \rho f \ddot{u}. \quad (5.4) \]

By virtue of (5.1) the internal and external mechanical powers are therefore given by

\[ P^i_m = \frac{1}{2} \frac{d}{dt} \left[ a (\triangle u)^2 + b (\nabla \dot{u})^2 \right] - c \theta \triangle \dot{u}, \quad P^e_m = -\nabla \cdot \mathbf{N}' + \rho f \dot{u}, \quad (5.5) \]

---

2 The representation (5.1) can be applied to a solid or liquid flow at small length scale and, with minor modifications, also to second grade nanocrystalline elastic materials [14].
where

\[ \mathbf{N}' = [a \nabla (\triangle u) - b \nabla \dot{u} - c \nabla \theta] \dot{u} - (a \triangle u - \theta) \nabla \dot{u}. \]

Consequently, the local form (5.11) of the First Law becomes

\[ \rho \frac{d}{dt} e = \frac{1}{2} \frac{d}{dt} \left[ a (\triangle u)^2 + b (\nabla \dot{u})^2 \right] - c \theta \triangle \dot{u} + \rho b \]

and it allows us to better understand the difference between the new formulation (1.5) and the classical one (1.1) proposed by Coleman [5] and Truesdell and Noll [36,34].

If, on the contrary, we want to keep the classical point of view, we must modify (1.1) by introducing a suitable extra flux \( \mathbf{N} \) and assume (1.7), as suggested by Dunn and Serrin [8]. In fact, taking into account (5.3)–(5.6) and (1.3), equation (5.7) assumes the form

\[ \rho \frac{d}{dt} e = -\frac{d}{dt} \left( \frac{1}{2} \rho \dot{u}^2 \right) + \rho f \dot{u} - \nabla \cdot \mathbf{N}' + \rho h = \mathbf{T} \cdot \nabla \dot{u} - \nabla \cdot (\mathbf{T} \dot{u} + \mathbf{N}') - \nabla \cdot \mathbf{q} + \rho r, \]

which coincides with (1.4) by choosing

\[ \mathbf{N} = (\mathbf{T} \dot{u} + \mathbf{N}') = -a \triangle u \nabla \dot{u}. \]

Let us now consider a thermoelastic plate with memory characterized by the following constitutive equation

\[ \mathbf{T}(t) = -\nabla \left[ \int_0^\infty C'(s) \triangle u^t(s)ds + C_0 \triangle u(t) \right] + c \nabla \theta(t), \tag{5.8} \]

where the scalar kernel \( C' \) is a suitable smooth function and \( u^t(s) = u(t - s) \).

Reasoning in the same way as in the previous model, we evaluate the terms in the right-hand side of (5.8) making use of (5.8) and obtain

\[ \frac{d}{dt} \left( \frac{1}{2} \rho \dot{u}^2(t) \right) + \left[ \int_0^\infty C'(s) \triangle u^t(s)ds - c \theta(t) \right] \triangle \dot{u}(t) + \frac{C_0}{2} \frac{d}{dt} [\triangle u(t)]^2 \]

\[ = \nabla \cdot \left\{ \left( -\nabla \left[ \int_0^\infty C'(s) \triangle u^t(s)ds + C_0 \triangle u(t) \right] + c \nabla \theta(t) \right) \dot{u}(t) \right. \]

\[ + \left. \left[ \int_0^\infty C'(s) \triangle u^t(s)ds + C_0 \triangle u(t) - c \theta(t) \right] \nabla \dot{u}(t) \right\} + \rho f(t) \dot{u}(t). \]

Hence, it follows that the internal and external mechanical powers are given by

\[ \mathcal{P}_m^i(t) = \left[ \int_0^\infty C'(s) \triangle u^t(s)ds - c \theta(t) \right] \triangle \dot{u}(t) + \frac{C_0}{2} \frac{d}{dt} [\triangle u(t)]^2, \quad \mathcal{P}_m^e(t) = -\nabla \cdot \mathbf{N}'(t) + \rho f(t) \dot{u}(t) \]

where

\[ \mathbf{N}'(t) = \left\{ \nabla \left[ \int_0^\infty C'(s) \triangle u^t(s)ds + C_0 \triangle u(t) \right] - c \nabla \theta(t) \right\} \dot{u}(t) \]

\[ - \left[ \int_0^\infty C'(s) \triangle u^t(s)ds + C_0 \triangle u(t) - c \theta(t) \right] \nabla \dot{u}(t). \]

Now, using the formulation (1.5) of the First Law, we could define the internal heat power as follows

\[ \rho h(t) = \rho \frac{d}{dt} e(t) - \left[ \int_0^\infty C'(s) \triangle u^t(s)ds - c \theta(t) \right] \triangle \dot{u}(t) - \frac{C_0}{2} \frac{d}{dt} [\triangle u(t)]^2. \]

Finally, by choosing

\[ \mathbf{N}(t) = - \left[ \int_0^\infty C'(s) \triangle u^t(s)ds + C_0 \triangle u(t) - c \theta(t) \right] \nabla \dot{u}(t), \]

we can use also (1.4) as local form of the First Law.
Other interesting examples, for which the classical representation of the power, used in the First Law, does not coincide with the one following from a correct balance between the internal and external powers, meet in electromagnetism, in the study of phase transitions and also in other physical systems, as those describing processes of phase separation, for example, by means of Cahn-Hilliard’s equation \[2\].

Firstly, we consider a rigid electromagnetic system for which the classical expression for the First Law is given by

\[
\frac{d}{dt} e = \dot{B} \cdot H + \dot{D} \cdot E + J \cdot E - \nabla \cdot q + r, \tag{5.9}
\]

where \(E, H, D, B, J\) are the electric and magnetic fields, the electric displacement, the magnetic induction and the current density, respectively.

Equation (5.9) together with (1.3) leads to the classical definition of internal electromagnetic power

\[
P^i_{cl} = \dot{B} \cdot H + \dot{D} \cdot E + J \cdot E \tag{5.10}
\]

and thermal power

\[
h = \frac{d}{dt} e - \dot{B} \cdot H - \dot{D} \cdot E - J \cdot E. \tag{5.11}
\]

These relations hold for a large class of electromagnetic materials, such as classical dielectrics, conductors characterized by the Ohm Law, materials with memory, etc. [9]. In analogy with the mechanical systems, these materials are still called simple. However there exist meaningful examples of fairly common materials, for which (5.9) must be modified by changing the internal electromagnetic power \(P^i_{cl}\) or by introducing an extra flux as follows

\[
\frac{d}{dt} e = \dot{B} \cdot H + \dot{D} \cdot E + J \cdot E - \nabla \cdot q + r. \tag{5.12}
\]

To this purpose we recall that, as already shown in [12], in presence of superconducting materials it is necessary to use (5.12) with an extra flux proportional to the superconducting current.

Here we consider a dielectric with quadrupoles described by the following constitutive equations

\[
\begin{align*}
D &= \varepsilon_0 E - \varepsilon_1 \nabla E - \varepsilon_2 \nabla \cdot \nabla E, \\
B &= \mu H, \\
J &= 0,
\end{align*} \tag{5.13}
\]

where \(\varepsilon_0, \varepsilon_1, \varepsilon_2\) are suitable constants characteristic of the dielectric.

The evolution of the electromagnetic field is governed by the well known Maxwell equations which, in absence of currents, are

\[
\begin{align*}
\dot{D} &= \nabla \times H, \\
\dot{B} &= -\nabla \times E.
\end{align*}
\]

An immediate consequence of the previous equations is the balance law for the electromagnetic power, known as Poynting theorem,

\[
\dot{D} \cdot E + \dot{B} \cdot H = \nabla \times H \cdot E - \nabla \times E \cdot H = -\nabla \cdot (E \times H)
\]

which, taking into account the constitutive equations (5.13), becomes

\[
\frac{1}{2} \frac{d}{dt} \left[ \mu |H|^2 + \varepsilon_0 |E|^2 + \varepsilon_1 |\nabla E|^2 + \varepsilon_2 |\nabla \cdot E|^2 \right] = -\nabla \cdot \left[ E \times H - \varepsilon_1 \nabla E - \varepsilon_2 \nabla \cdot \dot{E} E \right].
\]

Hence the expressions of the internal and external electromagnetic powers are

\[
\begin{align*}
P^i_{cl} &= \frac{1}{2} \frac{d}{dt} \left[ \mu |H|^2 + \varepsilon_0 |E|^2 + \varepsilon_1 |\nabla E|^2 + \varepsilon_2 |\nabla \cdot E|^2 \right], \\
P^e_{cl} &= -\nabla \cdot \left[ E \times H - \varepsilon_1 \nabla E - \varepsilon_2 \nabla \cdot \dot{E} E \right].
\end{align*}
\]
Consequently, the local form (3.11) of the First Law, with \( \mathcal{P}_m^t \) instead of \( \mathcal{P}_m^i \), becomes
\[
\frac{d}{dt} e = \frac{1}{2} \frac{d}{dt} \left[ \mu H^2 + \varepsilon_0 E^2 + \varepsilon_1 (\nabla E)^2 + \varepsilon_2 (\nabla \cdot E)^2 \right] + h
\]
and it allows us to give a properly definition of the thermal power \( h \) which does not agree with the classical definition (5.11).

Finally, it is easy to show that the relation (5.12) is satisfied by choosing
\[
\mathbf{N} = -\varepsilon_1 \nabla \hat{E} \mathbf{E} - \varepsilon_2 \nabla \cdot \hat{E} \mathbf{E}.
\]

Therefore, this example confirms that the local form (3.1) of the First Law (with \( \mathcal{P}_m^i \) instead of \( \mathcal{P}_m^i \)) has a universal character; on the contrary, (5.11) must be adapted in function of the material under consideration.

Let us now consider an example related to the phase transition in a binary mixture characterized by the Cahn-Hilliard equation
\[
\hat{c} = \nabla \cdot [M(c)\nabla \mu(c)],
\]
where \( c \in [-1,1] \) denotes the relative concentration of one of the two components, the mobility \( M \) represents the density with which the two phases are mixed and \( \mu \) is the chemical potential.

The mobility \( M \) is a nonnegative function and the chemical potential \( \mu \) is given by
\[
\mu(c) = -\gamma \Delta c + \theta_0 F'(c) + \theta G'(c),
\]
where \( \gamma \) is a positive constant, \( \theta_0 \) is the temperature of the transition, while \( G \) and \( F \) are the usual polynomials assumed for a second order transition, i.e.
\[
G(c) = \beta \frac{c^2}{2}, \quad F(c) = \beta \left( \frac{c^4}{4} - \frac{c^2}{2} \right), \quad \beta > 0.
\]

Therefore, from (5.14)–(5.16), we obtain
\[
\hat{c} = \nabla \cdot [M(c)\nabla (-\gamma \Delta c + \theta_0 F'(c) + \theta G'(c))].
\]

By multiplying (5.17) by the potential \( \mu \), we have the equation for the power
\[
\hat{\mu}(c) = \nabla \cdot [M(c)\mu(c)\nabla \mu(c)] - M(c) [\nabla \mu(c)]^2,
\]
which, by virtue of (5.18), can be rewritten as
\[
\theta_0 \hat{F}(c) + \theta \hat{G}(c) + \gamma \frac{d}{dt} (\nabla c)^2 + M(c) [\nabla \mu(c)]^2 = \nabla \cdot [\gamma \hat{c} \nabla c + M(c)\mu(c)\nabla \mu(c)].
\]

This relation allows us to define the internal and external chemical powers of the mixture
\[
\mathcal{P}^i_c = \theta_0 \hat{F}(c) + \theta \hat{G}(c) + \gamma \frac{d}{dt} (\nabla c)^2 + M(c) [\nabla \mu(c)]^2, \quad \mathcal{P}^e_c = \nabla \cdot [\gamma \hat{c} \nabla c + M(c)\mu(c)\nabla \mu(c)].
\]

If we put (5.18) into the heat equation
\[
\frac{d}{dt} e = \mathcal{P}^i_c = -\nabla \cdot \mathbf{q} + r,
\]
we get
\[
\frac{d}{dt} e = \hat{\mu}(c) + \gamma \nabla \cdot (\hat{c} \nabla c) + M(c) [\nabla \mu(c)]^2 - \nabla \cdot \mathbf{q} + r.
\]

It follows that if we want to use the usual expression \( \hat{\mu}(c) \) for the chemical power, even in this case, it is necessary to introduce the extra flux
\[
\mathbf{N} = -\gamma \hat{c} \nabla c.
\]

\[3\] Among the wide literature on the Cahn-Hilliard equation we recall, for example, [28] and [19] that set precedents.
We conclude this subsection by observing that if we take for the internal energy the constitutive equation
\[ e(\theta, c, \nabla c) = \theta_0 F(c) + \gamma \left( \nabla c \right)^2 + \tilde{e}(\theta), \]
then equation (5.19) assumes the following more usual form
\[ \frac{d}{d\theta} \tilde{e}(\theta) = \theta \dot{G}(c) + M(c) \left( \nabla \mu(c) \right)^2 - \nabla \cdot q + r. \]

A similar argument can be also applied to the binary mixture of two incompressible fluids studied by Lowengrub and Truskinovsky in [24].

5.1.2 Second Law of Thermodynamics

In this subsection we consider only non-simple materials in the heat flux, in other words, materials for which the constitutive equation for the heat flux depends also on the gradients of order higher than the first in the temperature.

For second grade materials, taking into account Definition 5.1, the internal virtual entropy action (4.2) becomes
\[ \tilde{A}_{en}^i(\sigma, P, \tilde{\gamma}_t) = \rho h(\sigma, P) \frac{1}{\theta_t} - q_1(\sigma, P) \cdot \nabla \left[ \frac{1}{\theta_t} \right] - q_2(\sigma, P) \cdot \nabla^{(2)} \left[ \frac{1}{\theta_t} \right]. \]

Inequalities (1.2) and (1.10) or, equivalently,
\[ \rho \frac{d}{dt} \theta \geq \frac{h}{\theta} + \frac{1}{\theta^2} q \cdot \nabla \theta \quad \text{for simple materials}, \]
\[ \rho \frac{d}{dt} \theta \geq \frac{h}{\theta} + \frac{1}{\theta^2} q \cdot \nabla \theta - \nabla \cdot \Phi' \quad \text{for non-simple materials}, \]
show that the Second Law assumes different expressions for simple or non-simple materials.

Reasoning in the same way as for the First Law, we suggest to claim the Second Principle in a unique general form through the inequality (1.17).

For simple materials the internal entropy action \( A_{en}^i \) is always given by the differential form of the right-hand side of (5.21), while the right-hand side of (5.22) cannot be taken as expression of \( A_{en}^i \) for non-simple materials, because of the presence of the external flux \( \nabla \cdot \Phi' \).

We now present an example [1] that helps to better understand the motivations of our suggestion. Let us consider a rigid heat conductor, whose constitutive equation is given by
\[ q(t) = q_1(\theta(t), \tilde{g}^t) - \nabla \cdot q_2(\theta(t), \tilde{g}^t, \nabla \tilde{g}^t) \]
where \( q_1 \) is a vector, \( q_2 \) is a second order tensor and \( \tilde{g}^t \) is the integrated history of \( \nabla \theta \), that is
\[ \tilde{g}^t(s) = \int_{t-s}^t g(\lambda) d\lambda. \]

The functional (5.23) is a typical constitutive equation of a second grade material; therefore, taking into account (5.20), the internal entropy action becomes
\[ A_{en}^i = \frac{1}{\theta^2} \left[ \theta h + q_1 \cdot \nabla \theta + q_2 \cdot \nabla^{(2)} \theta - \frac{2}{\theta} q_2 \nabla \theta \cdot \nabla \theta \right]. \]

Consequently, the First and Second Thermodynamic Laws have the following expressions:
\[ \frac{d}{dt} e = h, \]
\[ \frac{d}{dt} \eta \geq \frac{1}{\theta^2} \left[ \theta h + q_1 \cdot \nabla \theta + q_2 \cdot \nabla^{(2)} \theta - \frac{2}{\theta} q_2 \nabla \theta \cdot \nabla \theta \right]. \]

4 We can assume \( \rho = 1 \) without loss of generality.
We observe that, choosing
\[ \Phi' = -\frac{1}{\theta^2} \mathbf{q}_2 \nabla \theta, \]
the inequality \ref{eq:5.24} coincides with \ref{eq:5.25}.

Finally, we assume the following constitutive equations for the internal energy and heat flux
\[
e(\theta(t), \mathbf{g}^t, \nabla \mathbf{g}^t) = \tilde{e}(\theta(t)) + b(\mathbf{g}^t, \nabla \mathbf{g}^t),
\]
\[ \mathbf{q}_1(\theta(t), \mathbf{g}^t) = -\theta(t) \int_0^{\infty} K_1'(s) \mathbf{g}^t(s) ds,
\]
\[ \mathbf{q}_2(\theta(t), \mathbf{g}^t, \nabla \mathbf{g}^t) = -\theta(t) \int_0^{\infty} K_2'(s) \nabla \mathbf{g}^t(s) ds,
\]
with \( \tilde{e} \) positive and homogeneous function of \( \theta \), \( K_1 \) and \( K_2 \) smooth positive functions.

Then the internal entropy action becomes
\[
A_{en}^i(t) = \frac{1}{\theta(t)} \left[ h(t) - \int_0^{\infty} K_1'(s) \mathbf{g}^t(s) ds \cdot \nabla \theta(t) - \int_0^{\infty} K_2'(s) \nabla \mathbf{g}^t(s) ds \cdot \nabla^{(2)} \theta(t) \right] 
+ \frac{2}{\theta^2(t)} \int_0^{\infty} K_2'(s) \nabla \mathbf{g}^t(s) ds \nabla \theta(t) \cdot \nabla \theta(t)
\]
and the free energy potential \ref{eq:4.6} can be expressed as a sum of two terms
\[ \psi(\theta(t), \mathbf{g}^t, \nabla \mathbf{g}^t) = \psi_1(\theta(t)) + \psi_2(\mathbf{g}^t, \nabla \mathbf{g}^t), \]
where
\[ \psi_1(\theta) = \tilde{e}(\theta) - \theta \int_0^\theta \frac{1}{\tau} \frac{d}{d\tau} \tilde{e}(\tau) d\tau \]
and the functional \( \psi_2 \) satisfies the inequality
\[
\frac{d}{dt} \psi_2(\mathbf{g}^t, \nabla \mathbf{g}^t) \leq \int_0^{\infty} K_1'(s) \mathbf{g}^t(s) ds \cdot \nabla \theta(t) + \int_0^{\infty} K_2'(s) \nabla \mathbf{g}^t(s) ds \cdot \nabla^{(2)} \theta(t) 
- \frac{2}{\theta(t)} \int_0^{\infty} K_2'(s) \nabla \mathbf{g}^t(s) ds \nabla \theta(t) \cdot \nabla \theta(t).
\]

5.2 Other non-simple materials

It is worth to observe that there exist material systems, whose constitutive equations present higher order gradients, for which the internal mechanical virtual power and internal virtual entropy action are not covered by the expressions \ref{eq:4.11} and \ref{eq:4.12}.

For this purpose, let us consider the model proposed by Guyer and Krumhansl \cite{21} for the heat flux and recently studied in \cite{4, 32}. Since the constitutive law for heat flux is given by
\[
\dot{\mathbf{q}} + \frac{1}{\tau_R} \mathbf{q} = -c_V \nabla \theta + \tau_N [\nabla \mathbf{q} + 2\nabla (\mathbf{q} \cdot \mathbf{q})],
\]
(5.26)
it is easy to show that for this material the internal virtual entropy action cannot be represented in the form \ref{eq:4.2}. Anyway, we can still define the internal entropy action. In fact, if we choose
\[ c_V = \frac{c_0}{\theta^2}, \quad c_0 > 0, \]
and multiply \eqref{eq:5.23} by \( \mathbf{q} \), we obtain
\[
\frac{1}{\theta^2} \mathbf{q} \cdot \nabla \theta = -\frac{1}{c_0} \left[ \frac{1}{2} \frac{d}{dt} \mathbf{q}^2 + \frac{1}{\tau_R} \mathbf{q}^2 + \tau_N (\nabla \mathbf{q})^2 + 2 (\nabla \cdot \mathbf{q})^2 \right] + \frac{\tau_N}{c_0} \nabla \cdot (\nabla \mathbf{q} + 2 \nabla \cdot \mathbf{q} \mathbf{q}).
\]
(5.27)
The heat equation for a rigid conductor together with (5.27) yields

\[ \frac{1}{\theta} \frac{d}{dt} \theta - \frac{1}{2c_0 \tau_R} q^2 - \frac{1}{c_0 \tau_R} \left( \nabla q \right)^2 = -\nabla \cdot \left( \frac{q}{\theta} \right) + \rho \frac{r}{\theta} - \frac{\tau_N}{c_0} \nabla \cdot (\nabla q q + 2 \nabla \cdot q q). \]

Hence, the expressions of the internal and external entropy actions are given by

\[ A_{en}^i = \frac{1}{\theta} \frac{d}{dt} \theta - \frac{1}{2c_0 \tau_R} q^2 - \frac{1}{c_0 \tau_R} \left( \nabla q \right)^2, \]
\[ A_{en}^e = -\nabla \cdot \left( \frac{q}{\theta} \right) + \rho \frac{r}{\theta} - \nabla \cdot \Phi_0', \]

where

\[ \Phi_0' = \frac{\tau_N}{c_0} (\nabla q q + 2 \nabla \cdot q q) \]

and the Second Law of Thermodynamics (1.17) becomes

\[ \frac{d}{dt} \eta \geq \frac{1}{\theta} \frac{d}{dt} \theta - \frac{1}{2c_0 \tau_R} q^2 - \frac{1}{c_0 \tau_R} q^2 - \frac{\tau_N}{c_0} \left( \nabla q \right)^2 + 2 \left( \nabla \cdot q \right)^2. \] (5.28)

The previous inequality imposes restrictions on the constitutive equation (5.27). In fact, if we choose the following expression for the entropy

\[ \eta = \int_0^\theta \frac{1}{\tau} \frac{\partial e}{\partial \tau} d\tau - \frac{1}{2c_0} q^2, \]

then from (5.28) we obtain that the inequality

\[ \frac{1}{c_0 \tau_R} q^2 + \frac{\tau_N}{c_0} \left( \nabla q \right)^2 + 2 \left( \nabla \cdot q \right)^2 \geq 0 \]

must be satisfied for any field \( q \) and therefore the constitutive coefficients \( \tau_R \) and \( \tau_N \) must be positive.

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