On non-equilibrium entropy in continuum thermodynamics of materials with memory [1]

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BASED ON PREVIOUS WORKS of the author, the fundamentals of some basic concepts and methods currently used in the formulation of constitutive equations for linear or non-linear dissipative materials are revisited. The principles of the local state – or local equilibrium state – frequently used as the basis of Thermodynamics of Irreversible Processes in connection with the problem of the definition of a non-equilibrium entropy – are discussed, with emphasis laid on materials with memory exhibiting – as in linear or non-linear viscoelasticity – a delayed response to a constant loading. An adiabatic relaxation experiment is defined, from which it is shown that the usual formulation of the local state principle is too strong, since the set of relations which holds in equilibrium, and which makes use of macroscopic variables only, can never be applied without modification out of equilibrium. The same holds for the non-equilibrium Gibbs equation generally associated with the corresponding formalism when written with the real stress and temperature involved in the process. For dissipative behaviour of the differential type of order one, called also Markovian behaviour, a non-equilibrium entropy can be defined and some of the equilibrium relations can be applied to non-equilibrium situations. From this, a basic thermodynamic classification of rheological behaviour is obtained. In the non-Markovian case, the results are applied to the method of internal variables. A criterion for identifying suitable internal variables is obtained. They should correspond to Markovian behaviour when directly stimulated.

1. Introduction

EXPERIMENTAL EVIDENCE concerning the delayed response of most real materials and its coupling with physical and chemical effects, has been obtained since the pioneering experiments of BUFFON [10] in the eighteenth century with the delayed fracture of wood, those of VICAT [88] (the discoverer of the fundamentals of the hardening of cement) with the creep of iron, and a few years later the study of the creep of silk, glass, and silver threads by other authors. Since that time, it has been found that such effects can appear, with magnitudes depending on each specific case and environment, in all materials. Formulation in a realistic and consistent fashion of the corresponding three-dimensional constitutive equations and criteria, and evaluation of the risk of deterioration under long term evolution, still

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[1] The paper partly develops an invited lecture given to the 31th Solid Mechanics Conference in Mierki, Poland, in September 1996 [57].

remains a widely open problem, while the need is continuously increasing with the development of new techniques and new materials [4, 43, 47, 48, 50]. This is also needed in the development and application of numerical simulations techniques taking into account the real microstructure of the material and the interactions with the climatic and chemical changes in the framework of statistical continuum micro-mechanics [58, 45, 46, 48–51, 81]. From this viewpoint, the usefulness of Thermodynamics in providing a consistent framework for constitutive laws has been emphasized many times.

The thermomechanical aspects of material behaviour is often considered in the framework of Continuum Thermodynamics – also called Rational Thermo-dynamics. The latter was mainly developed in the fifties and sixties by NOLL, TRUESDELL *et al.* [71, 83–85], COLEMAN [16, 17], BRUN [8, 9], DAY [18] and others, through an approach directly derived from the works of CLAUSIUS [14, 15], MASSIEU [65] and DUHEM [23, 24] in a rather axiomatic form. In this approach, use is made of macroscopic variables for which the memory effects can be dealt with in the form of functionals of the history, first introduced by BOLTZMANN [6], and then developed by VOLTERRA [89–91], FRÉCHET [25] and others. In partic-ular, the use of such history functionals is well adapted to materials endowed by experimental evidence with continuous spectra of response times, as experimen-tally found on many real materials devoid of aging [34–36, 2, 3, 32, 26, 78] (also adressed using fractional calculus [1, 82]) or with aging due to chemical reactions occuring under load as in the case of cement concrete [3, 4]. In this approach by functionals, the existence of various thermodynamic functions is postulated, the justification being left to the consequences of the theory.

By contrast, the chemical and physical phenomena are most often considered in the framework of the Thermodynamics of Irreversible Processes (TIP) [59], itself being based on the efforts performed in the forties and fifties [66, 73–75] to extend the powerful formalism elaborated by GIBBS [30] for Equilibrium Thermodynamics. In TIP, it is accepted only as an approximation to take as non-equilibrium thermodynamic functions the very ones already defined for the case of equilibrium and/or reversible processes, this expressing the so-called "principle of local equilibrium", or "principle of the local state", in which the use of the so-called Gibbs equation plays a central role. From this, the range of validity of the approach is considered limited to the case qualified as "sufficiently near equilibrium", for which linear complementary equations are derived through a Taylor expansion limited to the first order [73–75, 59], the theory being extended to history-dependent behaviour through the use of internal or hidden variables [5, 2, 79, 57].

Thus, in order to include the chemical and physical aspects in the continuum-thermomechanics theory, one may have to combine theoretical formalisms of var-ious origins based on seemingly incompatible statements. Some of the associated

problems and discussions were presented in specialised symposia [22, 56]. This paper considers some of these problems on the basis of our previous attempts to ensure compatibility [37–42, 44]. For the sake of clarity and self-containment, Section 2 to 4 below recall the fundamental features of these two approaches. Section 5 comes back to discussing the principle of the local state by providing, for the case of finite deformations, a refined version of the derivations first presented in [37, 39]. From this, Section 6 provides a status of the non-equilibrium entropy for a specific class of behaviour called Markovian and provides a full thermodynamic theory for this class. Section 7 applies the obtained results to the method of internal variables frequently used for approximating non-Markovian behaviour, providing a criterion for the choice of internal variables. Section 8 compares the approach used in the paper with those used for the same problem by two other authors. The results are recapitulated in Section 9, which provides an exhaustive thermodynamic classification of material behaviour and proposes a physical interpretation.

2. Universal relationships of Continuum Thermodynamics

2.1. Conservation equations in global form

Continuum Thermodynamics starts by stating a set of universal relationships, valid for every materials and bodies, and which express conservation equations for mass, momentum, moment of momentum and energy. Their original form is a global one which relates mechanical and physical variables defined on any finite part of the body to its environment. We consider an open domain D with mass M, momentum B, moment of momentum L and the total (internal plus kinetic) energy E, and which may experience a movement relatively to matter, or for which some matter may flow across its boundary ∂D. Denoting by x the coordinates of a material point, ν its velocity $\dot{x}$, and ν_Σ the velocity of the corresponding geometric point on the moving boundary ∂D, the global conservation equations at time t are:

$$(2.1) \qquad M' \equiv \frac{\delta M}{\delta t} = \int_{\partial D} \rho(\nu - \nu_\Sigma) \cdot n d\Sigma,$$

$$(2.2) \qquad B' \equiv \frac{\delta B}{\delta t} = \int_D F^d dV + \int_{\partial D} \{P + \rho\nu(\nu_\Sigma - \nu) \cdot n\} d\Sigma,$$

$$(2.3) \qquad L' \equiv \frac{\delta L}{\delta t} = \int_D x \wedge F^d dV + \int_{\partial D} x \wedge \{P + \rho\nu(\nu_\Sigma - \nu) \cdot n\} d\Sigma,$$

(2.4) $$U' + C' = \int\limits_{D} (F^d \cdot \nu + r)dV$$

$$+ \int\limits_{\partial D} \{P \cdot \nu + h + (\rho u + \rho \nu \cdot \nu)(\nu_\Sigma - \nu) \cdot n\}d\Sigma.$$

In these equations,

(2.5) $$G' = \frac{\delta D}{\delta t} = \frac{\partial G}{\partial t} + \nu_\Sigma \cdot \operatorname{grad} G.$$

denotes the total time derivative of any quantity G in any material or imma-
terial movement of the domain, (.) the once contracted tensor product, $\wedge$ the
vector product, U and C the total internal and kinetic energies, respectively.
The volume and surface densities F^d, P, r, h denote the – assumed to be regular
– external volume forces, surface tractions, non-mechanical volume and surface
energy supplies (heat), respectively. The above equations are valid either for the
whole body, or for every subdomain inside it, or still for every superdomain in-
cluding the body and a part of its environment. For a closed body or domain with
boundary impervious to matter or following its movement, the time derivatives
involved in this equations become the material derivative:

(2.6) $$\dot{G} = \frac{dG}{dt} = \frac{\partial G}{\partial t} + \nu \cdot \operatorname{grad} G.$$

The above conservation equations are then supplemented by additional re-
lationships expressing the second Principle of Thermodynamics and involving
additional physical variables, temperature and entropy.

2.2. Global Clausius inequality and entropy

Historically, the Second Principle of Thermodynamics – or Carnot-Clausius
Principle – was, from the work of CARNOT [13] and after acceptance of the energy
conservation principle now known as the First Principle, originally expressed by
CLAUSIUS [14, 15] in his own notation, as the following weak inequality, globally
valid for any system in every evolution forming a closed cycle of the control
variables:

(2.7) $$\oint \frac{dQ}{T} \leq 0.$$

Here dQ is the increment of heat provided to the body during the time interval
dt while T denotes the empirical temperature at time t. The equality to zero is
obtained for reversible processes or behaviour, while the inequality is strict for

all other cases, characterised by irreversible processes or behaviour. After some delay, this led CLAUSIUS [15] to introduce a new physical quantity, which he called the entropy S, having the property that, for *reversible* processes or behaviour in a closed cycle of the controlled variables, the above inequality becomes the equality:

$$(2.8) \qquad \oint \frac{dQ}{T} = \oint dS = 0,$$

making thus entropy a function of state (understood as the set of controlled variables), this giving, for every reversible evolution between the initial state 0 and the present state 1:

$$(2.9) \qquad \int_0^1 \frac{dQ}{T} = S - S_0.$$

For irreversible evolutions between the two states, CLAUSIUS writes, Eq. (71) of his original 1865 memoir [15], denoted (C71) in the following:

$$(C71) \qquad N = S - S_0 - \int_0^1 \frac{dQ}{T},$$

where N is a quantity which should be positive for every irreversible process or behaviour, and which vanish for all reversible processes. It is thus the total amount of entropy produced within the body during its irreversible evolution. Of course, the above equation can also be written:

$$(2.10) \qquad S = S_0 + \int_0^1 \frac{dQ}{T} + N,$$

This relationship (C71) was derived from a modified form of the Carnot principle by considering that there exists at least one reversible process through which the body can be brought back from its present state to its initial state. Considering the closed cycle thus obtained, Clausius wrote:

$$(2.11) \qquad \int_0^1 \frac{dQ}{T} = -N < 0,$$

which is consistent with the first inequality written above.

Clausius obtained from this his Eq. (C71) by taking account of the vanishing of the entropy production during the reversible return process. The necessity of having such a reversible path led most physicists to state that entropy is not

defined – strictly speaking – in non-equilibrium situations. On the other hand, some physicists and most continuum mechanicists consider that the thermodynamic quantities, and in particular entropy, can be taken as primitive quantities of the theory, *a priori* defined also in non-equilibrium situations [11, 85, 83]. This has been questioned especially for entropy, seemingly without achieving mutual agreement up to now, see for instance [59].

In fact, taking the time derivative of Eq. (2.10) gives:

$$(2.12) \qquad \dot{S} = \frac{d}{dt}\left(\int_0^1 \frac{dQ}{T}\right) + \frac{dN}{dt},$$

showing that the original equation (C71) of Clausius can be considered as the first historical expression – in an integrated form – of an entropy balance equation if the existence of a non equilibrium entropy is to be accepted.

2.3. Local forms of the universal balance equations at regular points

For subdomains devoid of non-integrable singularities in the mechanical or physical variables, it is possible to express $M, B, L, U,$ and S through the integrals of the corresponding local densities, denoted, per unit mass, ρ, ν, u and s, respectively. For the entropy produced in an irreversible change between times 0 and, one may write:

$$(2.13) \qquad N = \int_0^1 Z(u)\,du,$$

Z being the global entropy production rate, expressed in terms of the local density one ζ by:

$$(2.14) \qquad Z = \int_D \zeta\,dV,$$

this expressing the additivity property of the entropy production. The balance equation (2.12) then becomes:

$$(2.15) \qquad \dot{S} = \int_D \left(\zeta + \frac{r}{T}\right)dV + \int_{\partial D} \frac{h}{T}\,d\Sigma.$$

This, together with the global forms of Subsec. 2.1 and the use of the classical divergence and transport theorems makes it possible to obtain the classical local forms of the universal balance equations at every regular point inside the body

through a localisation procedure based on the consideration of a dense family of homogeneous domains around a given material point. Denoting the specific volume by $\tau = 1\rho$, the universal balance equations in local form reduce eventually, in Euler variables, to:

$$(2.16) \qquad \rho\dot{\tau} = \operatorname{div}\nu\,,$$

$$(2.17) \qquad \rho\dot{\nu} = F^d + \operatorname{div}\sigma\,,$$

$$(2.18) \qquad \sigma^T = \sigma\,,$$

$$(2.19) \qquad \rho\dot{u} = \sigma : d + r - \operatorname{div}q\,,$$

$$(2.20) \qquad \rho\dot{s} = \zeta + \frac{r}{T} - \operatorname{div}\frac{q}{T}\,.$$

In the above expressions, all densities are functions of x and t. A similar localisation procedure applied to subdomains involving interfaces leads to a corresponding set of jump relationships at every point of an interface, see for instance [27, 51]. Considering that Clausius inequality must remain valid for every domain with vanishing volume around a given point, it is postulated in addition that the density of the entropy production rate ζ is non-negative at all times, giving:

$$(2.21) \qquad \zeta \geq 0\,,$$

the inequality being strict for all irreversible processes or behaviour and the equality to zero for reversible transitions or behaviour only.

Most often (the formalism proposed in [39 – 42] being one of the exceptions), the entropy balance (2.20) is not directly used as a general field equation of the problem, temperature and entropy being involved at the level of constitutive equations only. After appropriate transformation, Clausius inequality is used as providing restrictions on the possible forms that can be taken by these constitutive equations.

2.4. Universal expressions for the entropy production and dissipation densities

Entropy balance equation (2.20) may be considered as providing a universal expression for the entropy production rate ζ:

$$(2.22) \qquad \zeta = \rho\dot{s} - \frac{r}{T} + \operatorname{div}\frac{q}{T}\,.$$

Developing the divergence of the quotient in the R.H.S. of Eq. (2.22) makes it possible to split this expression for into two parts:

(2.23) $$\zeta = \rho\dot{s} - \frac{r}{T} + \operatorname{div} q + q \cdot \operatorname{grad} \frac{1}{T} \equiv \zeta_M + \zeta_T,$$

with

(2.24) $$\zeta_T = q \cdot \operatorname{grad} \frac{1}{T}$$

and

(2.25) $$\zeta_M = \rho\dot{s} - \frac{1}{T}(r - \operatorname{div} q).$$

It is generally postulated that ζ_T and ζ_M are non-negative separately.

Eliminating the heat supply between Eqs. (2.18) and (2.25) provides us with universal expressions for the mechanical part ζ_M of the entropy production and for Clausius inequality,

(2.26) $$\zeta_M = \rho\dot{s} - \frac{1}{T}(\rho\dot{u} - \sigma : \dot{\varepsilon}) \geq 0.$$

In Lagrange variables, valid for finite deformations as well as for small strains, it reads, in terms of the entropy density per unit initial volume, as:

(2.27) $$\zeta_M = \dot{S} - \frac{1}{T}\dot{U} + \frac{\Pi}{T} : \dot{\Delta} \geq 0.$$

Defining as usual the local dissipated power $\mathcal{D}$ per unit volume, also called *dissipation*, as:

(2.28) $$\mathcal{D} = T\zeta_M,$$

and taking account of Eq. (2.27), provides us with an universal expressions for the dissipation together with a corresponding form of the local Clausius-Duhem inequality in terms of the internal energy. In Lagrange variables, it becomes:

(2.29) $$\mathcal{D} = -(\dot{U} - T\dot{S} - \Pi : \dot{\Delta}) \geq 0.$$

The relationships (2.27) and (2.29) are not constitutive properties: derived from the universal balance equations, they are valid for every material and every behaviour, dissipative or not, once entropy has been defined for non-equilibrium situations.

3. Constitutive equations in the Equilibrium Thermodynamics Formalism

3.1. Extended Gibbs space and Gibbs equilibrium surface

In all classical formalisms of continuum thermomechanics, the constitutive equations are a set of equations by which the set of universal equations must be supplemented in order to determine the whole thermomechanical behaviour, namely displacements and stress distribution with their time evolution, of a body of finite size under external loadings and appropriate boundary conditions. In contradistinction to the conservation equations, that hold for every materials, these constitutive equations are not universal, but are specific to the material from which the body is made.

Considering perfect fluids with mechanical variables limited to volume V and pressure p, GIBBS [29, 30] showed that all the constitutive equations of a homogeneous medium in its various states of thermodynamic equilibrium can be represented by the geometric properties of a hypersurface in an affine hyperspace.

For a material which can be solid, the mechanical variables are the strain tensor Δ, which corresponds to the scalar variable V, and the stress tensor Π, which corresponds to the scalar variable $(-p)$. When the materials contains n chemical constituents involving thermal, mechanical and chemical phenomena only, we get an extended Gibbs hyperspace with $8+n$ dimensions. The properties at thermodynamic equilibrium are fully determined by a hypersurface, which is a $7+n$- dimensional manifold when the symmetry of the tensor Δ is taken into account. This hypersurface may be called the equilibrium surface or the extended Gibbs surface and is denoted Σ in the sequel. It is defined by a fundamental equation expressing the entropy as a function of the strain tensor Δ, the internal energy U per unit volume and the number of moles N_k of each constituent k:

$$(3.1) \qquad S = \underset{\sim}{S}\,(\Delta, U, N_1, \dots, N_n).$$

The fact that the thermal gradient has not to be involved in the thermodynamic functions when the temperature is not uniform has been shown by various authors [16, 18, 83, 85].

3.2. Properties of entropy at equilibrium and in reversible changes

As is known, in case of elastic materials without chemical changes expressed in the entropy representation, the properties of entropy at equilibrium or in reversible changes can be recapitulated as follows:

i) Entropy is a state function of Δ and U, that is, possible states in the extended Gibbs space (Δ, U, S) lie on a surface of this space (equilibrium surface property);

ii) the whole (thermo-elastic) behaviour is completely determined by the explicit knowledge of the fundamental equation expressing the specific entropy S in terms of the set (Δ, U) of independent variables;

(3.2)
$$S = \underset{\sim}{S}(\Delta, U) ;$$

iii) entropy is a potential for $1/T$ and $-\Pi/T$:

(3.3)
$$-\frac{\Pi}{T} = \frac{\partial \underset{\sim}{S}}{\partial \Delta} ,$$

(3.4)
$$\frac{1}{T} = \frac{\partial \underset{\sim}{S}}{\partial U} ;$$

iv) a Gibbs equation holds in macroscopic variables, that is:

(3.5)
$$\dot{S} = \frac{1}{T}\dot{U} - \frac{\Pi}{T} : \dot{\Delta} ;$$

v) various reciprocity relations, analogous to the well known Maxwell relations of the classical thermodynamics of homogeneous fluid phases and expressing in fact the Schwarz theorem on the crossed second partial derivatives hold;

vi) reversible accessibility from one state (one point on the equilibrium surface in the extended Gibbs space) to another state holds;

vii) the second differential of S in terms of (Δ, U) is negative definite;

viii) sets of independent variables can be interchanged and give equivalent formalisms by means of duality, involving various Legendre transforms.

In the reversible case, the constitutive equations are equations of state, relating for instance Π to (Δ, U), and which should be distinguished from the fundamental equation. When the set of derived equations of state is incomplete, there are usually many compatible ways of completing it, giving some freedom of expression for the missing equations of state and thus for the choice of the fundamental equation. The converse is not true: when the fundamental equation is given explicitly, the equations of state are fully defined and may be written in one way only. When a system evolves from one equilibrium state to another, the entire set of total variations of the different thermodynamic quantities experienced by the system at the end of the evolution is completely well defined if the equilibrium surface is assumed to be known. This is the case whether the evolution is reversible or not, provided that the initial and final states are both equilibrium states.

However, the equilibrium surface in the space (Δ, U, S) is generally considered to be not able to provide information about phenomena which occur during an irreversible evolution, nor does it indicate which (perhaps new) quantities could be defined to describe these phenomena. In particular, if entropy is not to be defined in out-of-equilibrium situations in terms of the variables (Δ, U), there is no way to describe the process in the extended Gibbs space (Δ, U, S). This may make rather paradoxical the classical statement, already proposed by Clausius [15], that the entropy of an isolated system – i.e. with constant (Δ, U) – tends towards a maximum which is obtained when the equilibrium is reached:

"Energie der Welt ist constant. Entropie der Welt strebt einem Maximum zu!"

Which entropy of the Universe Clausius had in view if it is not defined in an isolated system out of equilibrium? This was already questioned by Meixner, who stated that the use made by Clausius of the entropy concept for non-equilibrium situations was without justification [67].

We shall see below that this question can in fact be directly answered for a wide class of behaviour containing most classical models without or with internal variables. Before doing this, we consider the significance and limits of two frequently invoked corner stones of TIP: the local state principle and the fundamental Gibbs equation.

4. The basic concepts of the TIP formalism

4.1. The Local State Principle

In order to be a able to make use of thermodynamics in non-equilibrium situations, the viewpoint adopted in the Thermodynamics of Irreversible Processes is that a medium in non-uniform conditions must be considered as the union of a number of subdomains in homogeneous condition, and the various possible exchanges or interactions between these must be examined, each subdomain being itself supposed to be in a homogeneous state which is governed by the laws of thermodynamics for equilibrium states, see [66, 73–75, 31, 21, 33, 53, 59] and others.

In case of non-uniform conditions, each of these subdomains is considered as the infinitesimal volume element. Each infinitesimal volume element is taken to be in a homogeneous state, so that, since the necessary condition for thermodynamic equilibrium is thus satisfied, it can be considered, at least heuristically, as a homogeneous element in thermodynamic equilibrium governed by the laws of classical thermodynamics and their associated concepts, magnitudes and equations. It is then examined how these elements react between themselves by considering the irreversible processes which appear within the system as resulting from (thermodynamic) mutual imbalance.

These irreversible phenomena generally take the form of flux – i.e. transfer of measurable quantities – passing through the surfaces surrounding the element of volume considered and tending to re-establish mutual equilibrium. They appear in connection with gradients expressing the difference of state between two adjacent elements: temperature gradient for thermal conduction, potential difference for electric conduction, concentration gradient for the diffusion of a gas, to cite the simplest cases. Then, the tools of Equilibrium Thermodynamics are used for these situations thanks to introducing a set of additional assumptions [74, 75, 21, 31, 53, 59] generally expressed as follows:

For a system which is not in equilibrium, it is assumed (or postulated or supposed) that:

1. locally the same quantities and thermodynamic functions (internal energy, entropy, temperature, free energy, ...) exist as those defined in the system in thermodynamic equilibrium;

2. these quantities are expressed in the same way as if the system were locally in equilibrium;

3. in particular, thermodynamic functions such as internal energy, entropy, free energy, ..., so defined, are independent of the rate of the transformation.

While its original authors named this set of statements the "local equilibrium hypothesis", some authors have named it more recently the "Principle of the local state", see [53], p. 211 of the 1979th issue, [27, 28]. The origin of this terminology is perhaps to be found in the memoir by PRIGOGINE [74], p.18 of the French translation [75] where it is mentioned that the "local" expression for the Second Principle has to be opposed to its "global" expression, used in classical Thermodynamics, due to the fact that the coupling between the irreversible processes is possible only when they intervene in the same region of the system. This statement of locality is then said to be the central postulate on which the whole book is based. But, what is visible from the localisation procedure used in Continuum Thermodynamics, this does not imply the assumptions 1, 2, 3 presented above.

4.2. The fundamental Gibbs equation

Another basic ingredient of TIP is the use of the Gibbs equation, validity of which is postulated even for non-equilibrium conditions. In p. 103 of the memoir by PRIGOGINE [75], this is expressed in the following fashion (re-translated from the French):

"The main concern of Irreversible Thermodynamics is to assess the entropy production from the Gibbs equation. ...(This) constitues a new postulate, on which the whole TIP is based".

"The physical significance of this basic formula is that, even in non-equilibrium

situations, entropy depends on the same variables as those which characterise an equilibrium process."

"This is certainly not true anymore far from equilibrium".

For fluid systems with constant chemical composition under uniform pressure p and temperature T, the Gibbs equation is written as for the equilibrium case, Eq. (3.8) p. 19 of [75]:

$$(4.1) \qquad dS = \frac{1}{T}dU + \frac{p}{T}dV \,,$$

which, taking as usual positive sign for tension stress, would have the following form for solids in three dimensions:

$$(4.2) \qquad \dot{S} = \frac{1}{T}\dot{U} - \frac{\Pi}{T} : \dot{\Delta} \,.$$

Then, the consideration of two subsystems at different temperatures in diathermal contact leads to the conclusion that the rate of entropy production is a bilinear form in the heat flow rate and the temperature difference, a conclusion similar to the one obtained for ζ_T in the Rational Thermodynamics approach when passing from the finite difference to a gradient. The same approach is used for systems with chemical reactions for which the Gibbs equation is postulated in the form:

$$(4.3) \qquad dS = \frac{1}{T}dU + \frac{p}{T}dV - \sum_\gamma \frac{\mu_\gamma}{T}dN_\gamma \,,$$

where N_γ is the mole number of constituent $\gamma(\gamma = 1, \dots, m)$ and μ_γ its chemical potential defined, according to GIBBS [30] and DE DONDER [19] by:

$$(4.4) \qquad \mu_\gamma = -T\frac{\partial S}{\partial N_\gamma} = \frac{\partial U}{\partial N_\gamma} \,.$$

On the other hand, the entropy production increment is introduced in terms of the chemical reaction increment $d\xi_C$ and the chemical affinity A in the form [19]:

$$(4.5) \qquad d_iS = \frac{1}{T}Ad\xi_C > 0 \,,$$

$d\xi_C$ being itself defined as the degree of growth of the reaction, linked to the stoichiometric coefficients ν_γ by

$$(4.6) \qquad dN_\gamma = \nu_\gamma d\xi_c \,.$$

Then it is stated that the affinity A is a function of the state expressed in terms of the chemical potentials μ_γ by

(4.7)
$$A = -\sum_\gamma \nu_\gamma \mu_\gamma.$$

with the property that it should be zero at equilibrium.

Of course, postulating a Gibbs equation in the form (4.3) for non-equilibrium situations implies that existence of non-equilibrium entropy has also been postulated since it is involved in the Gibbs equation, assumed to be still valid in such situations. Since no other definition has been given to entropy in non-equilibrium situations, this means that, in TIP, entropy is considered as a primitive quantity, just as in Rational Thermodynamics. Thus, the non-equilibrium entropy has the same postulated status in both approaches.

5. A criterion of validity for the local state principle: the adiabatic relaxation experiment

5.1. The adiabatic relaxation experiment in macroscopic variables

If the local state principle is considered to be valid, it should be checked first in the case for which macroscopic variables are used only. We consider here the simplest situation, in which no change in the chemical composition of the body is involved. Using the entropy representation, the equilibrium fundamental equation is Eq. (3.2). In the right-hand side of this equation, the set of arguments (Δ, U) can be controlled experimentally, not only in the case of equilibrium but in every situation, including the irreversible ones, since:

• the deformation Δ can be imposed by a mechanical system;

• the heat flow inwards or outwards can also be controlled (by more or less insulating wall and heating devices), which determines U when Δ is fixed.

In addition, if the set (Δ, U) is fixed at a certain time (which implies adiabaticity from this time onwards), the system will tend spontaneously towards internal equilibrium if it has not already reached this state. This is an adiabatic relaxation experiment.

Since, for fixed chemical composition, U and Δ can be controlled at will, it can be said that the internal energy and the deformation are meaningful thermodynamical quantities even out of equilibrium.

Moreover, during the relaxation experiment, they have the same meaning and numerical values out of equilibrium as they have once the relaxed thermodynamic equilibrium is reached at the end of the adiabatic relaxation process. Entropy, however, is different.

5.2. The growth of entropy in delayed adiabatic relaxation

Let us consider again, in the extended Gibbs space (Δ, U, S), the extended hypersurface Σ of equilibrium states, or fundamental surface, discussed in Sec. 3. If, during a change from one equilibrium state to another, the value of the set of governing independent variables (Δ, U) changes from (Δ_1, U_1) to (Δ_2, U_2), S varies between two equilibrium values S_1 and S_2 which depend only on (Δ_1, U_1) and (Δ_2, U_2), and not on the path taken in the (Δ, U)-space to travel from (U_1, Δ_1) to (U_2, Δ_2). When the path is reversible, S is defined all along the path and its representative point in the (Δ, U, S) space has its trajectory necessarily contained in the equilibrium surface Σ during the whole process. In the traditional approach, this requires in addition the path to be covered at an infinitely slow speed.

However, the path in the (Δ, U)-space may also correspond to an irreversible process, during which the representative point in the (Δ, U, S)-space may – at least as a provisional working assumption - leave from the equilibrium surface Σ if we assume the entropy being still defined during this process, for instance through a functional of the history of (Δ, U) [16, 18]. Then, it is clear that the properties defined by the equations in Subsec. 3.2 above, being geometrical properties of the Σ surface, will no longer hold for such functionals, which jeopardizes the validity of the principle of local state as stated in Subsec. 4.1 above.

Let us consider now that some process takes the point M representing entropy in the (Δ, U, S)-space, from an initial equilibrium state (Δ_0, U_0, S_0) on the equilibrium surface to a point (Δ_1, U_1, S_1) outside this surface. Then, let us perform an adiabatic relaxation from the point (Δ_1, U_1, S_1). From this point onwards, the system is thermodynamically insulated. Its entropy can only increase as the system tends towards thermodynamic equilibrium defined by the point with coordinates $(\Delta_1, U_1, S_1^{eq})$ on the equilibrium surface Σ. Final thermodynamic equilibrium means that all the variables that can be defined on the system, including stress and temperature, do not change anymore, which is not the case, by definition, in retarded relaxation. Since entropy production is the only possible change of entropy during adiabatic relaxation, and since it should be strictly positive in the retarded relaxation, the point M is really outside Σ if the relaxation is retarded. Moreover, all points outside the surface Σ which are accessible from any initial point (Δ_0, U_0, S_0) are necessarily on one and the same side relatively to it.

A point like (Δ_1, U_1, S_1), being situated outside the equilibrium surface, is inaccessible by a reversible path (which might be used as a return path if it would exist), contrarily to the requirement stated by Clausius for defining entropy in non-equilibrium situations. This is a version of the BRIDGMAN paradox [7] underlined several times by KESTIN [55] for the case of plasticity.

5.3. A necessary condition of validity for the local state principle in macroscopic variables

Conversely, a necessary condition for the principle of local state, as enunciated in Subsec. 4.1, to be valid in macroscopic variables is that $S = S_1^{eq} = S^{eq}(\Delta_1, U_1)$ at all times during the adiabatic relaxation, i.e. that the adiabatic relaxation is isentropic. Since an adiabatic relaxation can be introduced at any time and at any point of a non-equilibrium process, a necessary and sufficient condition for this relaxation to be isentropic is that the dissipative evolution occurs within the equilibrium surface Σ in the extended Gibbs space Δ, U, S. However, since it has just been admitted that this cannot happen if the adiabatic relaxation is retarded, an instantaneous relaxation is a *necessary* condition for having an isentropic adiabatic relaxation. It must be noted that this last condition *is not, a priori,* sufficient to ensure that the instantaneous adiabatic relaxation is isentropic: it is quite possible at first sight to envisage an instantaneous adiabatic relaxation showing an instantaneous jump in entropy from (Δ_1, U_1, S_1) out of Σ to $(\Delta_1, U_1, S_1^{eq})$ on Σ. This important point will be especially examined in Subsec. 6.1. To summarize, adiabatic relaxation provides three conditions, each of which is sufficient to invalidate the local state principle:

A material does not obey the principle of local state in macroscopic variables if at least one of the following conditions is true:

• *the adiabatic relaxation is not isentropic;*

• *some trajectories representing the process in the extended Gibbs space may take place outside the equilibrium surface;*

• *the adiabatic relaxation is not instantaneous.*

5.4. Non-equilibrium Gibbs equation in macroscopic variables and the two Principles of Thermodynamics

For irreversible processes, the Clausius-Duhem inequality is strict and has, from Eq. (2.27) of Sec. 2, the form:

$$(5.1) \qquad \frac{1}{T}\dot{U} - \frac{\Pi}{T} : \dot{\Delta} < \dot{S},$$

for all irreversible processes, i.e for all $\dot{U}$ and $\dot{\Delta}$, independently of the fact that it would take place on the equilibrium surface or not. For reversible processes, the inequality becomes an equality which reads:

$$(5.2) \qquad \frac{1}{T}\dot{U} - \frac{\Pi}{T} : \dot{\Delta} = \dot{S}.$$

From Subsec. 3.2, this coincides with the Gibbs equation when written in the entropic representation in macroscopic variables.

The two relationships (5.1) and (5.2) are incompatible. Thus, when using the strain and internal energy only as macroscopic independent variables, a Gibbs equation written in the same form as in equilibrium cannot hold for dissipative solids, using the real non-equilibrium values of stress and temperature involved in the irreversible process. Hence, TIP cannot be based on the whole set of statements recalled in Subsecs. 4.1 and 4.2 above when these variables are used. At least one of these statements have to be relaxed or modified in order to have a consistent theory.

6. A status for the non-equilibrium entropy

6.1. Instantaneous entropy recovery and 2nd Principle for materials of the Markovian type

From a purely mechanical point of view, a material which can relax instantaneously at constant temperature is one for which the stress at the time t can only be a function of the present values at the same time t of the governing variables and their rates, and perhaps – as in the RIVLIN-ERICKSEN behaviour models [77] – of its right-time derivatives of higher order up to some finite one:

$$(6.1) \qquad \Pi = \underset{\sim}{\Pi} \left(\Delta; \dot{\Delta}; \ddot{\Delta}; \dots ; \Delta^{(n)}; T \right).$$

In this subsection, we consider that the time derivatives of the first order only are involved in the dependence of Π and T upon the governing variables. Taking the latter as (Δ, U), we consider the class of materials for which the stress tensor and the temperature are of the form, at every instant t:

$$(6.2) \qquad \Pi = \underset{\sim}{\Pi} \left(\Delta, U; \dot{\Delta}, \dot{U} \right),$$

$$(6.3) \qquad T = \underset{\sim}{T} \left(\Delta, U; \dot{\Delta}, \dot{U} \right).$$

To avoid any possible confusion, attention is drawn to the fact that such constitutive equations are not proposed here as substitutes for other modes of representation of the behaviour of real materials, as the ones that we shall consider later on in Subsec. 6.2 and Sec. 7.

Materials with stress expressed by Eq. (6.1) are called materials of the differential type [85, 18]. Materials with behaviour defined by Eqs. (6.2) and (6.3) are materials of the differential type in some extended sense on the one hand, since the dependence upon the time derivatives of U is also involved, and more restricted on the other hand since the rate dependence is limited to the order one. All along this paper, we refer more briefly to the class of behaviour defined by Eqs. (6.2) and (6.3) as *Markovian behaviour*, an expression borrowed

from CALLEN [11] (we used this terminology without the order one restriction in [37, 38, 39, 40].

For example, classical models of Markovian behaviour are the viscous and Kelvin models of linear viscoelasticity, the rigid-plastic, Bingham and Norton-Hoff models of viscoplasticity and the Eyring model of chemical kinetics (see for instance [47, 48]). In particular, the rigid-plastic behaviour is indeed Markovian since the stress is a homogeneous function of order zero in terms of the strain rate.

Markovian behaviour exhibits instantaneous relaxation: at some instant of t an irreversible evolution corresponding to non-zero values of the time derivatives of Δ and U, Π and T differ from their equilibrium value at this time. If Δ and U are then kept fixed at their value already reached at time t – so that their first and higher right derivatives are set to zero (adiabatic relaxation experiment) – there is a sudden change from the values $\Pi(t^-), T(t^-)$ of Π and T to their values $\Pi(t^+), T(t^+)$, with:

$$(6.4) \qquad \Pi(t^+) = \underset{\sim}{\Pi}(\Delta, U, 0, 0) = \underset{\sim}{\Pi}^{eq}(\Delta, U),$$

$$(6.5) \qquad T(t^+) = \underset{\sim}{T}(\Delta, U, 0, 0) = \underset{\sim}{T}^{eq}(\Delta, U).$$

Since the equilibrium values of Π and T are reached instantaneously, the same must hold for the entropy, assumed to exist in non-equilibrium, and which, at the worse, must be thus of the form:

$$(6.6) \qquad S = \underset{\sim}{S}(\Delta, U; \dot{\Delta}, \dot{U}; \ddot{\Delta}, \ddot{U}; \ldots; \Delta^{(p)}, U^{(q)}),$$

with the orders p and q of the highest-order derivatives being finite and with the equilibrium value given by:

$$(6.7) \qquad S(t^+) = \underset{\sim}{S}(\Delta, U; 0, 0; 0, 0; \ldots; 0, 0) = S^{eq}(\Delta, U).$$

We make use now of a classical argument due to COLEMAN [16] and previously to DEFAY [20, 76]. From Eq. (6.6), the time derivative of the entropy has the form:

$$(6.8) \qquad \dot{S} = \frac{\partial \underset{\sim}{S}}{\partial \Delta} : \dot{\Delta} + \frac{\partial \underset{\sim}{S}}{\partial \dot{\Delta}} : \ddot{\Delta} + \ldots + \frac{\partial \underset{\sim}{S}}{\partial \Delta^{(p)}} : \Delta^{(p+1)}$$
$$+ \frac{\partial \underset{\sim}{S}}{\partial U} \dot{U} + \frac{\partial \underset{\sim}{S}}{\partial \dot{U}} \ddot{U} + \ldots + \frac{\partial \underset{\sim}{S}}{\partial U^{(q)}} U^{(q+1)}.$$

Substitution of Eq. (6.8) in the Clausius-Duhem Inequality (2.27) rewritten in its strict form gives:

$$
(6.9) \quad \left(\frac{\partial \underset{\sim}{S}}{\partial \Delta} + \frac{\Pi}{T} \right) : \dot{\Delta} + \frac{\partial \underset{\sim}{S}}{\partial \dot{\Delta}} : \ddot{\Delta} + \ldots \frac{\partial \underset{\sim}{S}}{\partial \Delta^{(p)}} : \Delta^{(p+1)}
$$

$$
+ \left(\frac{\partial \underset{\sim}{S}}{\partial U} - \frac{1}{T} \right) \dot{U} + \frac{\partial \underset{\sim}{S}}{\partial \dot{U}} \ddot{U} + \ldots + \frac{\partial \underset{\sim}{S}}{\partial U^{(q)}} U^{(q+1)} > 0.
$$

Since, by hypothesis, the entropy S is independent of $\Delta^{(p+1)}$ and $U^{(q+1)}$, which are independent right-derivatives, the first member of Inequality (6.9) is a linear form in $\Delta^{(p+1)}$ and $U^{(q+1)}$ which cannot remain non-negative for any values of these quantities unless their coefficients are zero. Thus the entropy S is independent of $\Delta^{(p)}$ and $U^{(q)}$. Since, from Eqs. (6.2) and (6.3), Π and T are assumed to be independent of $\Delta^{(p)}$ and $U^{(q)}$ for all p and q bigger than 1, the argument can be repeated for these latter variables. Working backwards to the terms in $\ddot{\Delta}$ and $\ddot{U}$, it is seen that S does not depend on any of the present derivatives of Δ and U. The expression (6.6) for the entropy out of equilibrium is thus reduced to:

$$
(6.10) \qquad\qquad S = \underset{\sim}{S} (\Delta, U).
$$

This means that, for Markovian behaviour, the entropy is dependent only on the present values of Δ and U, whatever their previous history may be, and whatever values their time derivatives may take. However, when the adiabatic relaxation is over, the entropy reaches its equilibrium value $S = \underset{\sim}{S}^{eq} (\Delta, U)$, so that, for consistency, the entropy out of equilibrium should be identified with its equilibrium value, for all values the rates $\dot{\Delta}, \dot{U}$ and of the governing independent variables may take in the process and how far from the equilibrium one may be:

$$
(6.11) \qquad\qquad S = \underset{\sim}{S} (\Delta, U) \equiv \underset{\sim}{S}^{eq} (\Delta, U).
$$

Hence, there can be no instantaneous jump in entropy for this behaviour, contrary to the provisional assumption made in Subsec. 5.3. All the processes related to a material with stress and temperature in the form of Eqs. (6.2), (6.3) must of necessarily take place, in the extended Gibbs space Δ, U, S, on the equilibrium surface Σ. This happens even if the path is runned at *a finite rate* of the governing independent variables Δ and U. Conversely, the problem of defining entropy out of equilibrium can now be solved in a precise way for Markovian behaviour:

For materials with Markovian behaviour, a non-equilibrium entropy S
may always be defined. It **must** be taken as the same function of the
strain tensor and internal energy as the equilibrium entropy S^{eq}.

6.2. General case of the instantaneous adiabatic relaxation followed by delayed relaxation

When the stress and temperature depend not only on the present values of
Δ and U and their right time first derivatives, but also on their past history
$H^-(\Delta, U)$, being of the form:

$$(6.12) \qquad \Pi = \underset{\approx}{\Pi} \left[\Delta, U; \dot{\Delta}, \dot{U}; H^-(\Delta, U) \right],$$

$$(6.13) \qquad T = \underset{\approx}{T} \left[\Delta, U; \dot{\Delta}, \dot{U}; H^-(\Delta, U) \right],$$

the assumed defined non-equilibrium entropy S should be – a priori – not only
a function of the present values of Δ and U and their time derivatives, but also
a history functional of Δ and U. Therefore, in this case S should a priori be
written as:

$$(6.14) \qquad S = \underset{\approx}{S} \left[\Delta, U; \dot{\Delta}, \dot{U}; \ddot{\Delta}, \ddot{U}; \ldots ; \Delta^{(p)}; \ldots ; U^{(q)} H^-(\Delta, U) \right].$$

Taking the time derivative gives:

$$(6.15) \quad \dot{S} = \frac{\partial \underset{\approx}{S}}{\partial \Delta} : \dot{\Delta} + \frac{\partial \underset{\approx}{S}}{\partial \dot{\Delta}} : \ddot{\Delta} + \ldots + \frac{\partial \underset{\approx}{S}}{\partial \Delta^{(p)}} : \Delta^{(p+1)}$$

$$+ \frac{\partial \underset{\approx}{S}}{\partial U} \dot{U} + \frac{\partial \underset{\approx}{S}}{\partial \dot{U}} \ddot{U} + \ldots + \frac{\partial \underset{\approx}{S}}{\partial U^{(q)}} U^{(q+1)} + \dot{\underset{\approx}{S}}_{\Delta U},$$

where $\dot{\underset{\approx}{S}}_{\Delta U}$ is the continuation functional expressing the rate of variation of S
from the moment when Δ and U are kept constant (i.e. during an adiabatic
relaxation). Thus, by the same line of reasoning as in Subsec. 6.1, cannot depend
on the time derivatives of Δ and U and must take the form:

$$(6.16) \qquad S = \underset{\approx}{S} \left[\Delta, U; H^-(\Delta, U) \right],$$

meaning that, if it exists, it should reduce to a function of the present values of
Δ and U and a functional of their previous history. Remark that, as explained
for instance in [51], the partial derivatives involved in Eq. (6.15) are not the
gradient involved in the Gateaux differential of the functional $\underset{\approx}{S}$, but only the
instantaneous partial derivatives, given by the value of this gradient at time t.

6.3. Consequences for the potential properties

From Eq. (6.16), the fundamental inequality reduces to

$$(6.17) \qquad \left(\frac{\partial \underset{\approx}{S}}{\partial \Delta} + \frac{\Pi}{T}\right) : \dot{\Delta} + \left(\frac{\partial \underset{\approx}{S}}{\partial U} - \frac{1}{T}\right) \dot{U} + \underset{\approx}{\dot{S}}_{\Delta U} > 0,$$

where Π and T are history functionals of Δ and U, and may or may not also depend on the present values of the rates $\dot{\Delta}$ and $\dot{U}$.

If Π and T do not depend upon these rates, being simply of the form:

$$(6.18) \qquad \Pi = \underset{\approx}{\Pi} \left[\Delta, U; H^-(\Delta, U)\right],$$

$$(6.19) \qquad T = \underset{\approx}{T} \left[\Delta, U; H^-(\Delta, U)\right],$$

(as is the case when instantaneous elasticity exists), then by re-applying the same argument, one obtains:

$$(6.20) \qquad \frac{\Pi}{T} = -\frac{\partial \underset{\approx}{S}}{\partial \Delta} \quad ; \quad \frac{1}{T} = \frac{\partial \underset{\approx}{S}}{\partial U} \quad ; \quad S \neq S^{eq} \quad ; \quad \underset{\approx}{\dot{S}}_{\Delta U} > 0,$$

where the first two equations correspond to the main result of COLEMAN in [16], see also [83]. For this reason, the class of behaviour defined by constitutive equations of the form (6.18), (6.19) has been named *Colemanian* [37–39].

However, if Π depends upon $\dot{\Delta}$ and T upon $\dot{U}$, then, taking into account the fact that $\frac{\partial \underset{\approx}{S}}{\partial \Delta}$ and $\frac{\partial \underset{\approx}{S}}{\partial U}$ cannot depend on these derivatives since S itself does not, one has:

$$(6.21) \qquad \frac{\Pi}{T} \neq -\frac{\partial \underset{\approx}{S}}{\partial \Delta} = \frac{\Pi^{eq}}{T^{eq}} \; ; \quad \frac{1}{T} \neq \frac{\partial \underset{\approx}{S}}{\partial U} = \frac{1}{T^{eq}} \; ; \quad S \neq S^{eq} \; ; \quad \underset{\approx}{\dot{S}}_{\Delta U} > 0.$$

That the potential properties expressed by Eqs. (6.20) are not of general validity, but correspond to a specific class of behaviour, was shown by MANDEL [61–64], and independently by HUET [37–39].

By contrast, for a Markovian behaviour, the relations (6.21) become:

$$(6.22) \qquad \frac{\Pi}{T} \neq -\frac{\partial \underset{\approx}{S}}{\partial \Delta} = \frac{\Pi^{eq}}{T^{eq}} \; ; \quad \frac{1}{T} \neq \frac{\partial \underset{\approx}{S}}{\partial U} = \frac{1}{T^{eq}} \; ; \quad S = S^{eq} \; ; \quad \underset{\approx}{\dot{S}}_{\Delta U} = 0$$

showing that entropy is not a potential for the non-equilibrium stress and temperature in this case despite the fact that S and S^{eq} are equal. However, the first

two equations of (6.22) follow trivially from the third since, from Eq. (6.11), one has:

$$(6.23) \qquad \dot{S} = \frac{\partial \underset{\approx}{S}}{\partial \Delta} : \dot{\Delta} + \frac{\partial \underset{\approx}{S}}{\partial U} \dot{U} = -\frac{\Pi^{eq}}{T^{eq}} : \dot{\Delta} + \frac{1}{T^{eq}} \dot{U} = \dot{S}^{eq},$$

so that they neither require nor express any new principle. Remark that the last Eq. (6.23) is the equilibrium Gibbs equation, always valid at equilibrium.

Consequently, from the results obtained in Subsecs. 6.1 and 6.2, *there is no non-equilibrium behaviour* each of which satisfies the *complete set* of rules given in Subsec. 4.1 to define the local state principle. It is possible to find various special classes of behaviour which each, in out of equilibrium conditions, satisfy some relation which was originally established within equilibrium, but these cases are mutually exclusive: for example, a class which satisfies (6.20) does not satisfy (6.22) and *vice versa*.

There are also certain types of dissipative behaviour, such as those defined by (6.17), which satisfy none of the characteristic relations of thermodynamic equilibrium in macroscopic variables: entropy is not a function of the present value of Δ and U (but depends also on their whole history), and the entropy is not a potential for the stress and temperature. To express the stress and the temperature, some additional terms have to be added to the entropy gradient in the (Δ, U) space, similar to what is done for instance in [51] using the free energy in the (Δ, T) space. Of course, the use of the latter presupposes the existence of the non-equilibrium entropy which is in discussion here.

7. Reducing hereditary behaviour to Markovian ones

7.1. The internal variables approach

Of course, the class of Markovian behaviour is not large enough to encompass all the classes of behaviour that can be observed in real materials. When macroscopic variables only are considered in the constitutive equations for materials with delayed response, history functionals are needed in order to express the stress in finite terms. However, except in the case of linear viscoelasticity without aging, the practical identification of these functionals rises many practical problems, and leads most often to unstable results. On the other hand, in order to extend the equilibrium thermodynamics formalism to the irreversible behaviour of solids, a powerful method has been progressively elaborated since about fifty years through the use of the so-called *internal variables* or *hidden variables* [66 – 68, 5, 79, 80, 53 – 55, 28, 63, 86, 87, 69, 70]. Initially, this method was based on the Thermodynamics of Irreversible Processes. In the entropy representation we are using here, it involves, in addition to the internal energy U and

the strain tensor Δ, a set $a = \{a_1, a_2, \ldots a_k, \ldots a_N\}$ of internal variables, that do not appear in the universal balance equations. Sometimes they are introduced through an appropriate analogy, the most well known being rheological models based on mechanical and electrical systems [79, 72]. The introduction of these internal variables is generally associated with a set of constitutive assumptions. For instance it is assumed that the stress tensor Π at time t is an ordinary function of the present values of (Δ, U, a) at the same instant t, but not of the rates. Furtherly it is supposed that the entropy S exists in non-equilibrium situations and that the function relating S to (Δ, U, a) is again the same as for equilibrium. In some cases, it is assumed that a Gibbs equation is still valid with this extended set of variables. From these assumptions, it is generally obtained that the entropy is again a potential for the stress divided by the temperature (this result coming from the most often assumed independence of Π on $\dot{\Delta}$, and thus being limited to the case with instantaneous elasticity as seen in Sec. 6.2 above). Finally, it is stated that the set of equations thus obtained must be complemented by a set of – linear or non-linear – rate equations on which, again, no other information is provided.

7.2. A criterion for the internal variables

From the discussion of the preceding sections, it follows that in the internal variables method, the entropy may be – without *a priori* assumption – given a meaning out of equilibrium by appropriately choosing the set of internal variables. To yield realistic results, the latter have to be be obtained by identifying the involved dissipative mechanisms and relating them in a way satisfying the characteristics of the experimental response and/or of the observed dissipative mechanisms identified in the microstructure of the material. Together with non-dissipative ones, these dissipative mechanisms can be considered as forming the elements of a sytem representing its macroscopic behaviour. Let us assume that they can be chosen in such a way that each of them is Markovian when disconnected from the others and directly stimulated. Then, from the results obtained in the above sections, entropy is well defined for each dissipative mechanism *even when they are under irreversible evolution at finite rate*. Moreover, it depends neither on the rates nor on the history of the involved variables, but only on their present values. Thus, using the additivity property of entropy, it can be stated [37, 40, 44] that the overall entropy density of the material is well defined and is a simple function of the present values of the governing set of variables (Δ, U, a) involving the macroscopic variables (Δ, U) and the set a of the internal variables:

$$(7.1) \qquad\qquad S = \underset{\sim}{S}(\Delta, U, a).$$

This means that all the transformations – including those performed at a

finite rate – take place in the equilibrium surface of the space (Δ, U, a, S) while the continuation functional of S corresponding here to the one considered in Sec. 6.2 vanishes:

$$(7.2) \qquad\qquad \underset{\approx}{\dot{S}}_{\Delta U a} \equiv 0.$$

Therefore, the preceding results supply a rule to ensure that the decomposition of the behaviour into internal mechanisms has been taken far enough to make possible the definition of an out of equilibrium entropy. For this, it is necessary and sufficient that the identified mechanisms have either reversible or Markovian behaviour when directly stimulated.

It can be verified from the literature that, even in the non-linear case (including plasticity, viscoplasticity and chemical kinetics), the dissipative mechanisms that are used in practice when applying this method are Markovian when directly stimulated. Although not explicitly formulated in general, this may explain why the internal variables approach has been found so successful.

In the adiabatic relaxation performed on the macroscopic variables as defined in Sec. 5.1, the internal variables only are allowed to change. Thus, in the macroscopic Gibbs space (Δ, U, S), each combination of fixed values taken by the internal variables define a hypersurface $\Sigma'(a)$. All these surfaces are situated on one and the same side of the equilibrium surface Σ.

8. Comparison with other approaches

8.1. The Kestin method of the Accompanying Equilibrium State

In view of providing a consistent thermodynamic theory – exempted of a postulated non-equilibrium entropy – for the study of irreversible systems out of equilibrium, a variant of TIP has been constructed by KESTIN [53–55] in the framework of the internal variables approach. In this theory, the Gibbs equation is still considered fundamental and taken as a starting point, but the idea that entropy and temperature are really defined out of equilibrium is rejected. The Principle of *local equilibrium*, or of *local state* is made more precise than in classical TIP by specifying that the considered equilibrium is some appropriately defined accompanying equilibrium state (AES) corresponding to *frozen values* of the internal variables. Then, the accompanying equilibrium state is used in order to define the *accompanying entropy* and the *accompanying temperature* of the system when the latter is not in thermodynamic equilibrium, i.e. when the internal variables at least are evolving at a finite rate. This is performed by assuming that entropy and temperature are taken as the ones defined on the AES. Corresponding reversible processes are defined. They are considered as occuring in a virtual *Gibbsian state space*, and not on the so-called "physical space" [55]. For Kestin, the Gibbsian state space is the space with dimensions

(ε, U, a), which in Lagrange coordinates needed for finite strains becomes here (Δ, U, a). It is then stated that the non-equilibrium states are defined in a wider space admitting the Gibbsian space as a subspace forming a base manifold of the former. It is emphasised that the *dependent* physical variables *differ* from the ones associated to the AES. It is also emphasised that the entropy is calculated by integration on the Gibbsian state space and not on the physical space (for the sake of clarity, it should be noted that the name "Gibbsian state space" of Kestin differs from the "extended Gibbs space" that we used in Sec. 3.2 above, since the latter includes the entropy while Kestin's Gibbsian state space does not).

In addition to the above assumptions, the Gibbs equation is again written, *but only for the values of the dependent variables involved in the accompanying equilibrium state.* Hence, this avoids the problem of defining the entropy of the body in non-equilibrium situation. This equilibrium Gibbs equation is then used in order to obtain an explicit expression for the entropy production by elimination of the internal energy rate between the Gibbs equation of the AES and the energy balance equation. Here again, it is stated that the set of equations thus obtained must be complemented by a set of – linear or non-linear – rate equations, on which no other information is provided.

It is clear from the above description that Kestin's AES is the one obtained at the end of an adiabatic relaxation experiment performed, not only on the macroscopic variables, but also on the dissipative mechanisms corresponding to the internal variables supposed to be directly stimulated (which in fact modifies the system itself since then the subsystems become disconnected and the internal distribution of stresses is changed: for example, it is impossible to maintain the same stress in the two components of a Maxwell model if the partial strains in each component, taken as the internal variables, are frozen from some later instant). Thus, the Gibbs equation used is again an equilibrium one, and not an out of equilibrium one. Moreover, if Kestin's relaxation of internal variables would involve production of entropy, the calculated entropy production would not be the one really involved in the non-equilibrium process, but a greater one.

But, as seen in the above Subsection, when all the internal dissipative mechanisms are supposed to be Markovian, a non-equilibrium entropy can really be defined for the whole system when the independent variables, including the internal ones, are experiencing evolutions at finite rates. This can be done without having to state that the internal variables are frozen. Moreover, the dissipation can then be directly evaluated without having to invoke the Gibbs equation, neither the detour of an Accompanying Equilibrium State: it is simply the sum of the dissipations of all the dissipative mechanisms.

8.2. The Valanis-Caratheodory method based on integrability of the first law

Another approach adressing the existence of entropy in the internal variables formalism has been used by VALANIS [86, 87] who extends to this case the non-accessibility theorem obtained by CARATHEODORY [12] for reversible processes. Caratheodory's theorem can be expressed by the fact that, when the supply of heat to a reversible system is prevented (adiabatic process), the previously chosen *independent* variables (Δ, U) of the reversible case cannot remain independent. This defines an hypersurface in the (Δ, U)-space and yields the integrability of the first law for reversible behaviour in adiabatic conditions (as shown in [86], Appendix II to Sec. 3). Therefore, adiabatic access to points outside this hypersurface of the (Δ, U)-space are forbidden. Moreover, the converse is also true.

In the extension to the non-reversible case made by Valanis, adiabatic processes with frozen internal variables are again considered, as in the work of Kestin mentioned above. Valanis considers the space (U, Δ, a) of the governing independent variables, which he calls the *thermodynamic state space*, which thus coincides in fact with the Gibbsian state space of Kestin, but not with our extended Gibbs space (U, Δ, a, S). As a basic axiom of the theory and a – somewhat restrictive – definition of irreversible behaviour, it is postulated that the stress tensor is a state function of (U, Δ, a) (and thus is independent of the rates). The integrability of the first law in this space is then proven when the internal variables are kept frozen, which gives both a definition of entropy and temperature as in the Caratheodory treatment of the reversible case. Potential properties, due again to the basic axiom of the theory postulating independence of Π from the rates of (Δ, U), are also obtained. The Carnot-Clausius Principle on the positive production of entropy is replaced by – and in fact deduced from – a postulate on the behaviour of the free energy in an isothermal relaxation experiment.

The problem of defining an entropy remaining meaningful during a real process is adressed, in the approach by Valanis, through the concept of *partial integrability* of the first law which, in fact, reduces again to keeping frozen the internal variables, the system becoming reversible in this situation (Sec. 4 of [87]).

By choosing explicitly the internal variables as relating to dissipative mechanisms that are Markovian, it seems possible to relax the restriction of frozen internal variables, making the entropy defined by Valanis also having a meaning when the internal variables are changing at finite rates, i.e. in every real process. Moreover, it suggests it might be possible to extend the basic axiom and mathematical derivations of the Caratheodory-Valanis theory to the case where the stress depends explicitly on the strain and internal energy rates in addition to the dependence upon the present values of (U, Δ, a), i.e. to materials devoid of instantaneous elasticity, providing thus, in the same framework, a direct definition of entropy for more general cases. But this is still an open question needing further research.

9. Conclusion

From the derivations performed in this paper, it can be stated that, depending on the form taken by the response to the adiabatic relaxation experiment, materials behaviour with delayed response falls into four mutually exclusive categories when using macroscopic variables only:

1. *Reversible behaviour which exhibits no adiabatic relaxation.*

2. *Markovian dissipative behaviour, for which the adiabatic relaxation is instantaneous.*

3. *Colemanian dissipative behaviour in which there is a delayed relaxation, either of the stress, or of temperature, or of both, but no instantaneous one.*

4. *General hereditary dissipative behaviour, where there is an instantaneous relaxation, either of the stress, or of temperature, or of both, followed by a delayed one.*

Reversible behaviour is governed by the classical thermodynamics of equilibrium and all its classical relationships. For some types of dissipative behaviour, it is possible to apply some of the equilibrium relations to some cases out of equilibrium, but then there are always other relations which cannot be directly applied.

For Markovian behaviour, a fundamental result is that *not only the reversible evolutions of a Markovian system take place on the equilibrium surface in the extended Gibbs space* (Δ, U, S), *but also their irreversible ones, whatever the magnitude of the rates – and thus whatever the distance reached from equilibrium – might be.*

In the non-Markovian case, the power of the method of internal variables with their mechanical or electrical analogs – appears to be connected with the fact that it is often possible to obtain a reduction to Markovian behaviour by introducing a sufficient number of suitable supplementary – "internal" or "hidden" – variables. *But the behaviour of a suitable internal variable must itself be reversible or Markovian when directly stimulated.*

From this, it appears possible to relax some restrictive assumptions and to enlarge the domain of validity of some of the theories using the internal variables approach while adressing also the problem of the existence of entropy in dissipative processes.

It has to be remarked that the above fundamental result concerning the dependence of entropy upon the macroscopic variables Δ and U only, as found for Markovian behaviour, means that instantaneous adiabatic relaxation – which corresponds to a change of mechanical state and is thus a real process – must be considered a reversible one. Effectively, since there is no change in the entropy and no supply of entropy from the exterior, there is no production of entropy

in the instantaneous adiabatic relaxation for Markovian behaviour. Thus the question arises if this can be given a direct physical meaning.

In fact, the above remark is consistent with the observation that every adiabatic *unloading* of a perfectly rigid body can itself be considered a reversible process, devoid of any dissipation since it involves neither expense nor release of work, and thus nothing to be converted into heat. Indeed, no deformation is associated with the instantaneous finite unloading of a body with Markovian behaviour, for instance of the viscous, Kelvin, Bingham or rigid-plastic types. Thus, every Markovian body appears as perfectly rigid under any finite instantaneous unloading, making non-dissipative the instantaneous relaxation process. Since all points of the equilibrium surface are connected by reversible paths, this provides the reversible return process required by Clausius in its original definition of entropy. This physically justifies the choice made in Secs. 6 and 7 of this paper for the definition of the non-equilibrium entropy for Markovian behaviour and answers the question raised at the end of Sec. 3.

Other consequences of the above discussion and other aspects of the thermodynamic theory of real materials dealt with by the author may be found in [40-52].

Acknowledgments

References

1. R. L. Bagley, P. J. Torvik, *On the fractional calculus of viscoelastic behaviour*, J. Rheology, **30**, 133–155, 1986.

2. Z. P. Bazant, *Theory of creep and shrinkage of concrete, a precis of recent developments*, [In:] S. Nemat-Nasser [Ed.], Mechanics Today, **2**, Pergamon, 1975.

3. Z. P. Bazant [Ed.], *Mathematical modeling of creep and shrinkage of concrete*, Wiley, 1988.

4. Z. P. Bazant, F. Kaplan [Eds.], *Concrete at high temperature: material properties and mathematical models*, Longman, 1996.

5. M. A. Biot, *Theory of stress-strain relation in anisotropic viscoelasticity and relaxation phenomena*, J. Appl. Phys., **25**, 11, 1385–1391, 1954.

6. L. Boltzmann, *Zur Theorie der elastischen Nachwirkungen*, Sitzungsber. Kaiserlich Akad. Wiss., Wien, Math. Naturwiss. Klasse. **70** (II), 275, 1874.

7. P. W. Bridgman, *The thermodynamics of plastic deformation and generalized entropy*, Rev. Modern Physics, **22**, 1, 56–63, 1950.

8. L. Brun, *Thermodynamique et viscoélasticité*, Cahiers du Groupe Français de Rhéologie, **I**, 4, SEDOCAR, Paris, 191–202, 1967.

9. L. BRUN, *Méthodes énergétiques dans les systemes évolutifs linéaires*, J. Mécanique, **8**, 125–166, 1969.

10. G. L. BUFFON, LE CLERC, Comte de, *Expériences sur la force du bois*, L'Académie Royale des Sciences, Histoire et mémoires, Paris, 453–467, 1740.

11. H. R. CALLEN, *Thermodynamics*, John Wiley and Sons, 6th Ed., New-York 1966.

12. CARATHEODORY, *Untersuchungen über die Grundlagen der Thermodynamik*, Math. Annalen, **67**, 355–, 1909.

13. S. CARNOT, *Réflexions sur la puissance motrice du feu et sur les machines propres a développer cette puissance*, Bachelier, Paris 1824.

14. R. CLAUSIUS, *On another form of the Second Principle of the mechanical theory of Heat*, Pogg. Ann., Décember 1854, French translation by R. Folie, in: "R. Clausius, Théorie Mécanique de la Chaleur", Mémoire IV, Lacroix, Paris 1865, 131–160.

15. R. CLAUSIUS, Sur diverses formes des équations fondamentales de la théorie mécanique de la chaleur qui sont commodes dans l'application, Journ. de Liouville, 2, X, 361 [In:] "R. CLAUSIUS, Théorie Mécanique de la Chaleur", Mémoire IX, Lacroix, Paris 1865, 377–420.

16. B. N. COLEMAN, *Thermodynamics of materials with memory*, Arch. Rational Mech. Anal., **17**, 1–46, 1964.

17. B. N. COLEMAN, V. J. MIZEL, *Existence of caloric equations of state in thermodynamics*, J. Chem. Phys., **40**, 1116–1125, 1964.

18. W. A. DAY, *The Thermodynamics of simple materials with fading memory*, Springer-Verlag, Berlin 1972.

19. TH. DE DONDER, *L'Affinité*, Gauthier-Villars, Paris 1931.

20. R. DEFAY, Bull. Ac. Roy. Belg. (Cl. Sc.), 347, 1938.

21. S. R. DE GROOT, P. MAZUR, *Non-equilibrium thermodynamics*, North-Holland, Amsterdam 1962.

22. J. J. D. DOMINGOS, M. N. R. NINA, J. H. WHITELAW (Eds), *Foundations of continuum thermodynamics*, MacMillan, London 1974.

23. P. DUHEM, *Le potentiel thermodynamique et ses applications a la mécanique chimique et à l'étude des phénomènes électriques*, Hermann, Paris 1886.

24. P. DUHEM, *Traité d'énergétique ou de thermodynamique générale*, 2 volumes, Gauthier-Villars, Paris 1911.

25. M. FRÉCHET, *Sur les fonctionnelles continues*, Ann. Sc., Paris, **27**, 3, 193–216, 1910.

26. C. FRIEDRICH, H. BRAUN, *Generalized Cole-Cole behaviour and its rheological relevance*, Rheologica Acta, **31**, 309–322, 1992.

27. P. GERMAIN, *Mécanique des milieux continus*, Masson, Paris 1973.

28. P. GERMAIN, *The role of thermodynamics in continuum mechanics*, [In:] J. J. D. DOMINGOS et al. [Eds.], Foundations of Continuum Thermodynamics, Mc Millan, London 1974, 317–333.

29. J. W. GIBBS, *A method of geometrical representation of the thermodynamic properties of substances by means of surfaces*. Trans. Connecticut Academy, II, 382–404, 1873.

30. J. W. GIBBS, *On the equilibrium of heterogeneous substances*. Trans. Connecticut Academy, **III**, 108–248 and 343–524, 1875.

31. P. GLANSDORF, I. PRIGOGINE, *Structure, stabilité et fluctuations*, Masson, Paris 1971.

32. P. GRESSEL, *Prediction of long term deformation behavior from short term creep experiments*, Holz als Roh-und Werkstoff, **42**, 8, 293–301, 1984.

33. E. A. GUGGENHEIM, *Thermodynamics*, North-Holland, Amsterdam 1967.

34. C. HUET, *Comportement viscoélastique d'un matériau hydrocarboné*, C. R. Ac. Sc. Paris, **257**, 1438–1442, 1963.

35. C. HUET, *Etude par une méthode d'impédance du comportement viscoélastique des matériaux hydrocarbonnés*, Annales des Ponts et Chaussées, Paris, **6**, 373–429, 1965.

36. C. HUET, *Représentation des modules et complaisances complexes dans les plans complexes arithmétique et logarithmique*, Cahiers du Groupe Français de Rhéologie, **1**, 5, 237–58, 1967.

37. C. HUET, *Sur la notion d'etat local en rhéologie*, Sciences et Techniques de l'Armement, Paris, **53**, 4, 611–651, 1979.

38. C. HUET, *Topics in thermodynamics of rheological behaviour*, Rheologica Acta, **21**, 360–365, 1982.

39. C. HUET, *Thermodynamique des comportements rhéologiques en variables naturelles*, Rheologica Acta, **22**, 245–259, 1983.

40. C. HUET, *Macroscopic rheology without functionals: the natural variables formalism*, [In:] B. MENA et al. [Eds.], Advances in Rheology, Mexico University Press 1984, 497–507.

41. C. HUET, *A new approach for the termodynamics of materials with delayed response*, [In:] H. D. BUI, Q. S. NGUYEN [Eds.], Thermomechanical Coupling in Solids, North-Holland, Amsterdam 1987, 37–42.

42. C. HUET, *Application of the natural variables formalism to classical rheological models*, [In:] P. H. T. UHLHERR [Ed.] Proc. Xth Int. Congress in Rheology, Sydney, Australia, vol. 1, 419–421, 1988.

43. C. HUET, *Modeling the kinetics of the thermo-hygro-viscoelastic behaviour of wood under constant climatic conditions*, [In:] R. ITANI [Ed.], Proc. International Conference on Timber Engineering, FPRS, Madison 1988, 395–401.

44. C. HUET, *Definition of the out of equilibrium entropy through the use of markoffian variables and the example of elasto-visco-plastic mechanical models*, [In:] J. KESTIN AND TH. LEHMAN [Eds.] "What is the Correct Form of the Gibbs Equation for Inelastic Deformations in Solid Bodies", Universität Bochum, 1988.

45. C. HUET, *An integrated approach of concrete micromechanics*, [In:] C. HUET [Ed.], Micromechanics of Concrete and Cementitious Composites, Presses Polytechniques et Universitaires Romandes, Lausanne 1993, 117–146.

46. C. HUET [Ed.], *Micromechanics of concrete and cementitious materials*, Presses Polytechniques et Universitaires Romandes, Lausanne 1993.

47. C. HUET, *Some basic tools and pending problems in the development of constitutive equations for the delayed behaviour of concrete*, [In:] Z. P. BAZANT AND I. CAROL [Eds.], Creep and Shrinkage of concrete, Spon, London 1993, 189–200.

48. C. HUET, *Recent advances in the long term deformation and deterioration behaviour of structural materials and components through the integrated micromechanics and thermodynamics of solids approach*, [In:] A. GERDES [Ed.] Advances in building materials, Aedificatio, Freiburg 1996, 161–196.

49. C. HUET, *Hybrid continuum thermodynamics framework and numerical simulations examples for the delayed micromechanical behaviour of heterogeneous materials with chemical, climatic and defects sensitivity*, [In:] Q. S. NGUYEN AND V. D. NGUYEN [Eds.], Engineering Mechanics Today, University of Hanoi 1995, 170–184.

50. C. HUET, *Continuum thermodynamics and microstructure-creep couplings in heterogeneous and/or microcracked materials: some recent general results and examples of application*, [In:] A. JAKOWLUK [Ed.], Creep and coupled processes, Bialystock Technical University Publishers, 1996.

51. C. HUET, *An integrated micromechanics and statistical continuum thermodynamics approach for studying the fracture behaviour of microcracked heterogeneous materials with delayed response*, Engineering Fracture Mechanics, **58**, 5-6, 459–556, 1997.

52. C. Huet and P. Navi, *Multiparabolic multitransition model for thermo-viscoelastic behaviour of wood*, [In:] ASME [Ed.] Mechanics of Woods and Paper Materials, Dallas, Texas. 17–24, 1990.

53. J. Kestin, *A course in Thermodynamics*, Hemisphere Publishing Comp., New-York; 2 vols., 1979.

54. J. Kestin, *Entropy and entropy production; discussion paper*, [In:] J. J. D. Domingos, M. N. R. Nina and J. H. Whitelaw [Eds.]. Foundations of Continuum Thermodynamics, Mc Millan, London 1974, 143–158.

55. J. Kestin, *Local-equilibrium formalism applied to mechanics of solids*, Int. J. Solids Structures, 29, 14/15, 1827–1836, 1992.

56. J. Kestin and Th. Lehman, [Eds.], *"What is the correct form of the Gibbs equation for inelastic deformations in solid bodies"*, Symposion Proceedings, Universität Bochum, 1988.

57. W. Kosinski, R. De Boer, D. Gross [Eds.], *Problems of environmental and damage mechanics*, Proceedings of the 31st Polish Solid Mechanics Conference, Mierki, IPPT, Warsaw 1996.

58. E. Kröner, *Statistical continuum mechanics*, Springer-Verlag, Vienna 1972.

59. D. C. Kuiken, *Thermodynamics of irreversible processes: Applications to diffusion and rheology*, Wiley, 1994.

60. J. Mandel, *Cours de mécanique des milieux continus*, Gauthier-Villars, Paris, 2 vols. 1966.

61. J. Mandel, *Application de la thermodynamique aux milieux viscoélastiques a élasticité nulle ou restreinte*, Comptes-rendus Ac. Sc. Paris, **264**, 133–134, 1967.

62. J. Mandel, *Introduction a la mécanique des milieux continus déformables*, Editions Scientifiques de Pologne, Warsaw 1974.

63. J. Mandel, *Variables cachées. Puissance dissipée. Dissipativité normale*, Sciences et techniques de l'armement, Paris 1979, **210**, 4, 525–538.

64. J. Mandel, L. Brun, *Thermodynamique et ondes dans les milieux viscoélastiques*, J. Mech. Phys. Solids, **16**, 33–58, 1967.

65. F. Massieu, *Sur les fonctions caractéristiques des divers fluides*. C. R. Acad. Sc., Paris, **69**, 858–862, 1869.

66. J. Meixner, *Zur Thermodynamik der irreversiblen Prozesse in Gasen mit chemisch ragierenden, dissozierenden und anregbaren Komponenten*, Annalen der Physik, **5**, 43, 244–270, 1943.

67. J. Meixner, *Entropy and entropy production*, [In:] J. J. D. Domingos *et al.* [Eds.] Foundations of Continuum Thermodynamics, Mc Millan, London 1974, 129–142.

68. J. Meixner, H. G. Reik, *Thermodynamik der irreversiblen Prozesse*, [In:] S. Flügge [Ed.], Encyclopedia of Physics, III/2, 23B, Springer, 413–523, 1959.

69. S. Nemat-Nasser, *On non-equilibrium thermodynamics of viscoelasticity and viscoplasticity*, [In:] J. J. D. Domingos *et al.* [Eds.], Foundations of Continuum Thermodynamics, Mc Millan, London 1974, 259–282.

70. S. Nemat-Nasser, *On non-equilibrium thermodynamics of continua*, [In:] S. Nemat-Nasser [Ed.], Mechanics Today, Pergamon, 2, 94–158, 1975.

71. W. Noll, *A mathematical theory of the mechanical behaviour of continuous media*, Arch. Rational Mech. Anal. **2**, 197–226, 1958.

72. B. Persoz, *Modeles non-linéaires*, [In:] B. Persoz [Ed.], La Rhéologie, Masson, Paris 1969.

73. I. Prigogine, *Etude thermodynamique des phénomènes irréversibles*, Desoer, Liege, Dunod, Paris 1947.

74. I. Prigogine, *Introduction to thermodynamics of irreversible processes*, Wiley, 1962.

75. I. Prigogine, *Introduction a la thermodynamicue des processus irreversibles*, Dunod, Paris 1962.

76. I. Prigogine, R. Defay, *Thermodynamique chimique*, Desoer, Liège 1950.

77. R. S. Rivlin, J. L. Ericksen, *Stress-deformation relations for isotropic materials*, J. Rational Mech. Anal. **4**, 323–425, 1955.

78. N. Ruddock, P. W. James, T. E. R. Jones, *Modelling the viscoelasticity of unfilled and carbon black elastomers*, Rheol. Acta, **32**, 286–292, 1993.

79. A. J. Staverman, P. Schwarzl, *Thermodynamics of viscoelastic behaviour (model theory)*, Proc. Acad. Sc., The Netherlands, **55**, 474–485, 1952.

80. A. J. Staverman, P. Schwarzl, *Non-equilibrium thermodynamics of visco-elastic behaviour*, Proc. Acad. Sc., The Netherlands, **55**, 486–492, 1952.

81. H. Sunderland, A. Tolou, C. Huet, *Multilevel numerical microscopy and tridimensional reconstruction of concrete microstructure*, [In:] C. Huet [Ed.] Micromechanics of Concrete and Cementitious Composites, Presses Polytechniques et Universitaires Romandes, Lausanne 1993, 171–180.

82. P. J. Torvik, R. L. Bagley, *On the appearance of the fractional derivative in the behaviour of real materials*, J. Appl. Mech., **51**, 294–298, 1984.

83. C. Truesdell, *Rational thermodynamics*, Mac Graw Hill, New-York, 1969.

84. C. Truesdell, R. Toupin, *The classical field theories of mechanics*, [In:] S. Flügge [Ed.] Encyclopedia of Physics, vol. III/1 Springer-Verlag (Berlin 1960).

85. C. Truesdell, W. Noll, *The non-linear field theories of mechanics*, [In:] S. Flügge [Ed.], Encyclopedia of Physics, vol. III/3, Springer-Verlag, 1965.

86. K. C. Valanis, *Irreversibility and existence of entropy*, Int. J. Non-Linear Mechanics, **6**, 337–360, 1971.

87. K. C. Valanis, *Partial integrability as a basis for the existence of entropy in irreversible systems*, ZAMM, **63**, 73–80, 1983.

88. L. J. Vicat, *Note sur l'allongement progressif du fil de fer soumis a diverses tensions*, Annales de Chimie et de Physique, Paris, **54**, 35–40, 1833.

89. V. Volterra, *Sopra le funzioni che dipendono da altre funzioni*, R. C. Accad. Lincei, **4**, 3, 97–105, 1887.

90. V. Volterra, *La théorie des fonctionnelles appliquées aux phénomenes héréditaires*, Rev. Gén. Sci. pur. appl., **41**, 197–206, 1930.

91. V. Volterra, *Theory of functionals and of integral and integro-differential equations*, 1925 Madrid Lectures, Dover, New-York 1959.