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Continuum Thermodynamics

Introduction

Fifty years ago, the term "continuum mechanics" was not widely used. A significant emphasis on continuum mechanics could be found in the postwar literature with Rivlin's and Truesdell's pioneering works. A few years later, it became clear to most scientists involved in this new field that thermodynamics should play a central role in continuum mechanics. If one may say that the importance of continuum mechanics significantly increased during the 1950s, one may assert that it is during the 1960s that continuum thermodynamics began to be a popular topic attracting the attention of numerous people.

Quite a number of great scientists had already introduced "continuum thermodynamics" in their work without using the word: for instance, Lord Rayleigh for viscous flows and Lord Kelvin for the thermoelectric effect. Special mention should be made of Duhem's work [1] which demonstrated a very clear view of the role of thermodynamics in continuum physics. At the time, his main ideas did not receive the attention they deserved. They are nevertheless present in Jouguet's and Roy's works. Other examples may be given in the field of chemistry: de Donder's work and the fundamental results of Onsager and Casimir provided the foundations on which the thermodynamics of irreversible processes (TIP) was built. The expansion of continuum thermodynamics in the 1960s is evidenced not only through the number of situations that have been considered but also by the widespread desire to deal with the field in its full generality, to exhibit the basic assumptions as well as the significance of the concepts involved, and hopefully, to derive methods that could be applied to any physical situation.

The expansion of continuum thermodynamics has raised many controversies during the last 20 years; they still persist at the present time[1]. A first line of thought, referred to as "rational thermodynamics," asserts that the introduction of thermodynamical concepts into the field of moving continuous media requires a complete rethinking and reformulation of classical thermodynamics which is primarily concerned with systems in equilibrium. A second line of thought maintains that the concepts should not be drastically changed. The former criticizes the lack of ambition and of intrepidity of the latter; it prefers to think of "entropy" and of "absolute temperature" as basic concepts similar to that of "forces" in dynamics. The second argues that these concepts have no physical content outside equilibrium and its neighborhood. Such important questions will receive some attention in the present paper but we will not take side in the controversy. It is, in our opinion, a new example of the diversity of preferences: on the one hand, the need for a clear and rigorous mathematical formulation, and on the other hand the desire to remain in close contact with physical reality. We prefer to emphasize what we consider to be the main objective of continuum thermodynamics, i.e., *the construction of models*[2] that *are as simple as possible and which can*:

(*i*) explain the qualitative behavior of various experimentally observed phenomena;

(*ii*) give rise to a quantitative evaluation which may be compared to measurements;

(*iii*) allow one to formulate well-posed mathematical problems and to study the solutions together with their evolution and stability for varying data.

To conclude this introduction we will briefly describe the main parts of the paper. The first section is devoted to the

[1] See for instance the recent discussions in the *Bulletin of the Institute of Mathematics and Applications*. References to these discussions are given in [2].
[2] We emphasize that we are concerned with *models*; we do not claim for them a universal validity.

basic equations. Section *II* is concerned with the concepts connected with the generalization of the second law. It will provide the opportunity to mention a few important questions and answers formulated in the spirit of rational thermodynamics. Section *III* describes the method of the "local accompanying equilibrium state" (l.a.s.) which will be used later in its most convenient version, i.e., when the constitutive equations may be obtained from two scalar valued convex functions: a thermodynamical potential and a pseudopotential of the dissipations. Some classical applications, mainly in solid mechanics, are given in Section *IV*. The concept of global state variables is introduced in Section *V*, and its interest is illustrated in relevant examples. Section *VI*, which is devoted to homogenization[3] and thermodynamics, provides some insight into the consistency of the l.a.s. model and into its physical interpretation by exhibiting the relations between descriptions at the microlevel and at the macrolevel. Finally, a few elements of bifurcation and stability theory are given in Section *VII*. They show that the model emphasized in this paper provides a first significant contribution toward what was called the third main objective.

I Basic Equations of Thermodynamics

1 A Few Remarks About Classical Thermodynamics. Classical thermodynamics is concerned with systems in equilibrium which usually may be characterized by a finite number of scalar quantities which define the state Σ of the system. Any thermodynamical property of the system is by definition represented by a function defined on the space V of states.

Classical thermodynamics exhibits properties that can be associated with any thermodynamical system as consequences of a few statements or laws: the empirical temperature θ by the "zeroth" law; by the first law, the internal energy E and the heat received by the system in a transformation or process between two states after interaction with the surroundings. *Reversible processes* may be represented by an arc drawn on V and all the thermodynamical functions attached to any point Σ of this arc have their usual physical significance. Consequently, the differential dE of E is the sum of two differential forms, the elementary work and the elementary heat received by the system during an elementary reversible process.

The second law has received a remarkably large number of forms, and discussions still continue to decide which one of these forms is optimal. Carathéodory's formulation rests on a statement of "inaccessibility" by adiabatic processes. It is then possible to prove that there exists a universal (absolute) temperature T and a universal entropy S such that $T\,dS$ is the elementary heat received in a reversible process. Moreover, for an adiabatic process $\Sigma_1 \rightarrow \Sigma_2$, it may be shown that $S(\Sigma_2) \geq S(\Sigma_1)$.

Some people say that classical thermodynamics has to be called *thermostatics* because it deals only with equilibrium states. Others disagree, noting that time is in fact implied in most of its classical definitions; namely it is true that the statement "such a system is in equilibrium" and the choice of the variables that characterize its state Σ depend on the characteristic time which is of interest for the observer. The work thermostatics is adequate if one restricts its use to case where *all* the properties associated with a state Σ of V—like E, S, and T for instance—have their full physical significance. The following example which gives a first idea of what will be called *internal variables* shows the nuance that may be introduced. Take a system [3] whose states Σ may be defined by E and deformation variables X_i. A continuous process (with time) may have an image on V—it is possible to define $E(t)$,

$X_i(t)$, and then $S(t)$. Generally, the function $S(\Sigma)$ will have no significance for such a process. But it may happen that this same process may be considered as a reversible one, when V is embedded in a "larger" space $\hat{V}$. The process may be looked upon as a thermodynamic one on V and as a thermostatic one on $\hat{V}$. Internal energy has the same significance (although different analytic expressions) in V and in $\hat{V}$; entropy may be defined only in $\hat{V}$, and $\hat{S}(\hat{\Sigma})$ has nothing to do with $S(\Sigma)$.

2 Basic Equations. We consider now a continuous material system Ω in motion with respect to an inertial frame R. The *basic equations* express the laws that fully describe the physical system independently of the special properties of the material. They always include the conservation laws of mass, momentum, and energy and when only thermomechanical interactions are involved, as is usual in classical continuum mechanics, these conservation laws are the basic equations. A conservation law is symbolically written for any subdomain D of Ω as:

$$\frac{d}{dt}\int_D \mathcal{Q}\,dv + \int_{\partial D} J_A\,d\sigma - \int_D \varphi_A\,dv = 0 \tag{1}$$

As is well known, [4], for a three-dimensional domain:

A is the quantity (a vector or a scalar) that is conserved per unit mass and $\mathcal{Q} = \rho A$ the quantity per unit volume; d/dt or $(\dot{\ })$ means the material derivative;

J_A is the *associated flux* (per unit area and per unit time);

φ_A is the *supply* (per unit volume and per unit time) that represents the action of the surroundings of Ω ($\varphi_A = \rho\,S_A$);

As a consequence:

J_A is linear in n (outer unit normal to ∂D), $J_A = j_A \cdot n$, j_A being the associated flux tensor or vector;

At each point of Ω, the following equation holds:

$$\rho\,\dot{A} + \operatorname{div} j_A - \varphi_A = 0 \tag{2}$$

At each point of a surface of discontinuity inside Ω, a jump relation may be written.

The conservation of energy is the natural extension of the first law of thermostatics; differences are replaced by material derivatives, work by power, heat by heat rate and kinetic energy is taken into account. The material derivative of the kinetic energy of D may be eliminated by application to the real motion of the virtual power statement and, consequently, the power $P_{(e)}$ of external forces on D disappears. Heat rate on D may be assumed (as $P_{(e)}$) to be the result of an associated flux J_Q and of a supply φ_Q. Finally, the equation (2) for energy may be replaced by:

$$\rho\,\dot{e} = \epsilon_{(i)} + \operatorname{div} j_Q + \varphi_Q, \tag{3}$$

where e is the internal energy per unit mass, $\epsilon_{(i)}$ the opposite of the power of internal forces (per unit volume) or the *energy (per unit volume) due to internal forces*. In (3) all the quantities involved are objective or frame indifferent.

(*i*) In *classical continuum mechanics* for an Eulerian representation

$$j_Q = -q, \quad \varphi_Q = r, \quad \epsilon_{(i)} = tr(\sigma \cdot D) \tag{4}$$

with D, the strain rate tensor or the symmetric part of the velocity gradient, and the conservation laws are symbolically written:

	$\mathcal{Q} = \rho A$	j_A	$\varphi_A = \rho\,S_A$
Mass	ρ	0	0
Momentum	ρv	$-\sigma$	f
Energy	$\rho\left(e + \frac{1}{2}v^2\right)$	$q - \sigma.v$	$f.v + r$

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[3]Homogenization is the modeling of a heterogeneous system by a continuum.

In a Lagrangian representation (x_i orthonormal Eulerian variables, $\hat{x}_\alpha$ orthonormal Lagrangian variables), the motion is described by:

$$x_i = \phi_i(\hat{x}_\alpha, t) \quad i, \alpha = 1, 2, 3 \tag{5}$$

A conservation law is written on a fixed domain in the reference configuration $\hat{R}$: A, S_A can again be used; but mass-density $\hat{\rho}$ (mass per unit volume of $\hat{R}$), quantities per unit volume of $\hat{R}$, flux vector or tensor $\hat{j}_A$ have to be changed in order to obtain an equation similar to (2). Similarly, in the Lagrangian version of (3), one has to write:

$$\hat{\epsilon}_{(i)} = tr(t \cdot \dot{L}), \quad \rho^{-1}\epsilon_{(i)} = \hat{\rho}^{-1}\hat{\epsilon}_{(i)} \tag{6}$$

with t the (second) Piola-Kirchhoff stress tensor and L the Green-Lagrange strain tensor.

(*ii*) When electromagnetic interactions have to be taken into account, one must include in the conservation laws the electromagnetic effects in the flux and supplies of momentum and energy, but also include among the basic equations the Maxwell equations, see for instance [5][4].

(*iii*) *Mixture of fluids* is another example which requires a refined description. Let us introduce a *balance equation*, similar to the conservation law (1) but including a production term on the right-hand side:

$$\frac{d}{dt}\int_D \mathcal{B} \, dv + \int_{\partial D} j_B \cdot n \, d - \int_D \varphi_B \, dv = \int_D \mathcal{B}^* \, dv \tag{7}$$

The supply φ_B comes from the surroundings of Ω; on the contrary $\mathcal{B}^* = \rho B^*$ is produced inside the system, and $\mathcal{B}^*$ is the rate of production per unit mass. The equations of balance of each constituent ($\lambda = 1,2\ldots\nu$) of the mixture are symbolically written (no summation with respect to λ):

$\mathcal{B} = \rho B$	j_B	φ_B	$\mathcal{B}^* = \rho B^*$
ρ^λ	0	0	τ^λ
$\rho^\lambda v^\lambda$	$-\sigma^\lambda$	f^λ	m^λ
$\rho^\lambda\left[e^\lambda + \frac{1}{2}(v^\lambda)^2\right]$	$q^\lambda - \sigma^\lambda \cdot v^\lambda$	$r^\lambda + f^\lambda \cdot v^\lambda$	l^λ

Conservation laws for the mixture as a whole implies:

$$\sum_{\lambda=1}^{\nu} \tau^\lambda = 0, \quad \sum_{\lambda=1}^{\nu} m^\lambda = 0, \quad \sum_{\lambda=1}^{\nu} l^\lambda = 0 \tag{8}$$

These global conservations may be written as previously with the following definitions:

$$\rho = \sum_{\lambda=1}^{\nu} \rho^\lambda, \quad \rho_v = \sum_{\lambda=1}^{\nu} \rho^\lambda v^\lambda, \quad u^\lambda = v^\lambda - v,$$

$$\rho e = \sum_{\lambda=1}^{\nu} \rho^\lambda\left[e^\lambda + \frac{1}{2}(u^\lambda)^2\right], \quad \sigma = \sum_{\lambda=1}^{\nu}(\sigma^\lambda - \rho^\lambda u^\lambda \otimes u^\lambda)$$

$$q = \sum_{\lambda=1}^{\nu}\left\{q^\lambda + \rho^\lambda\left[e^\lambda + \frac{1}{2}(u^\lambda)^2\right]u^\lambda - \sigma^\lambda \cdot u^\lambda\right\} \tag{9}$$

In particular (3) has to be written with $\varphi_Q = r = \Sigma_{\lambda=1}^{\nu}(r^\lambda + f^\lambda u^\lambda)$.

The u^λ are the diffusion velocities. If there are p chemical independent reactions with Λ^k, $k = 1,2\ldots p$, their reaction rate densities, if $\gamma^{\lambda,k}$ is the stoichiometric coefficient of constituent λ (molecular weight M_λ) in the reaction k, then

$$\tau^\lambda = \sum_{k=1}^{p}(\gamma^{\lambda,k}M_\lambda\mu)\Lambda^k \tag{10}$$

with 16μ the mass of the oxygen atom. Then the p rate densities Λ^k determine the ν mass production terms τ^λ.

What are the basic equations for a mixture? *Various answers are possible.* There is general agreement to accept the existence of *one* empirical temperature θ valid for the mixture and for all constituents; then it is natural to write only the global conservation law of energy. A first choice is to keep as basic equations the following $4\nu + 1$ scalar valued equations:

$$\left.\begin{aligned}
\dot{\rho}^\lambda + \rho^\lambda \, \text{div} \, v^\lambda &= \tau^\lambda \\
\rho^\lambda \dot{v}^\lambda - \text{div} \, \sigma^\lambda &= m^\lambda + f^\lambda \\
\rho \, \dot{e} &= tr\{\sigma \cdot D\} - \text{div} \, q + r
\end{aligned}\right\} \tag{11}$$

Another less refined but more classical choice is to take as basic equations the $\nu + 4$ equations written in (11) after replacing the ν momentum equations $(11)_2$ by the global momentum equation.

3 Constitutive Equations. When the basic equations have been chosen, one must analyze the quantities involved. Among these quantities, one has to identify those which will be chosen as *principal unknowns* (p.u.). Then in order to solve the problem, the *complementary unknowns* (c.u.) must be expressed through laws that describe the properties of the material: these laws are the constitutive equations. This can be explained by some examples.

In *classical continuum mechanics*, one may choose as the *principal unknowns* (p.u.) one of the following set according to the selected representation:

$$\left.\begin{aligned}
&[\rho(x_k, t), \quad v_i(x_k, t), \quad \theta(x_k, t)] \text{ or} \\
&[\rho(\hat{x}_\alpha, t), \quad \phi_i(\hat{x}_\alpha, t), \quad \theta(\hat{x}, t)]
\end{aligned}\right\} \tag{12}$$

The auxiliary unknowns[5] (a.u.) are the quantities that can be directly computed from the (p.u.): acceleration $\dot{v}$, deformation gradient F, strain rate tensor. . . Looking at the basic equations, one sees that the *complementary unknowns* (c.u.) are:

$$[e, \sigma, q] \quad \text{or} \quad [e, t, \hat{q}] \tag{13}$$

These (c.u.) —say C— must be expressed in terms of the (p.u.) by the constitutive functions that must fulfill some very well-known requirements: causality, localization, objectivity or material frame indifference[6], and material symmetry.

If one writes symbolically:

$$C(\hat{x}_\alpha, t) = \underset{t' \leq t}{\mathcal{F}}\left\{\Phi(\hat{x}_\alpha, t'), \theta(\hat{x}_\alpha, t'); \hat{x}_\alpha\right\} \tag{14}$$

$\mathcal{F}$ is a casual functional which depends on the history of the system up to (and including) time t. Note that the basic equations impose no further restriction on F: whatever be the values of the (p.u.), whatever be F, one can always check the equations by a convenient choice of the supplies f and r.

For a mixture of fluids ruled by the $(4\nu + 1)$ basic equations (11) the (p.u.) will be:

$$\rho^\lambda(x_k, t), \quad v_i^\lambda(x_k, t), \quad \theta(x_k, t) \tag{15}$$

and, the (c.u.) are:

$$e, \sigma^\lambda, q, m^\lambda, \Lambda^k; \quad \lambda = (1,2\ldots\nu), \quad k = (1,2\ldots\rho) \tag{16}$$

If the mixture is described by the less refined description with $\nu + 4$ equations, the (p.u.) and the (c.u.) will be, respectively:

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[4] This paper shows the usefulness of the method of virtual power in dealing with such complicated situations.

[5] As ρ may be directly computed from the ϕ_i or from the v_i, it is generally considered as an auxiliary unknown; in such a case mass conservation is not counted among the basic equations.

[6] Frame indifference of the constitutive equations is not always accepted in its full generality—see for instance [2]. Let us emphasize that the *models* considered in the present paper rest effectively on this *working assumption*. Experimental studies show that this working assumption may be used safely in most of the applications met by engineers.

$$\rho^\lambda, \, v_i, \, \theta; \quad e, \, u^\lambda, \, \sigma, \, q, \, \Lambda^k \qquad (17)$$

In each case the constitutive equations must relate the (c.u.) to the (p.u.) by functions or functionals that fulfill the aforementioned requirements.

II Entropy, Absolute Temperature, and Fundamental Inequality

Continuum thermodynamics impose new important restrictions on constitutive equations when a suitable generalization of the second law is formulated. The main objective of continuum thermodynamics is to provide a method to write constitutive equations that fulfill these new restrictions.

One may look at this generalization of the second law from many different points of view. In the following subsections, we will consider first the case where entropy and absolute temperature are more or less considered as primitive concepts, then the case when only entropy is a primitive concept, and finally we consider attempts to start without such assumptions.

1 Clausius Duhem Inequality. The First Version of Rational Thermodynamics.

In classical continuum mechanics, any time that specific entropy s and absolute temperature T have been defined or are considered as primitive concepts, everybody agrees to write the rate of production of entropy σ^* in the form:

$$\rho \, T \, \sigma^* = \epsilon_{(i)} + \rho(T \dot{s} - \dot{e}) - q \cdot \nabla(\log T) \qquad (18)$$

when $\epsilon_{(i)}$ has been defined in (4). Note that no *supply is involved* in (18). Clausius Duhem inequality, which is an expression of the second law, says that σ^* and then the right-hand side of (18) is *non-negative*.

The first version of rational thermodynamics [6], considers s and T as primitive concepts. An admissible process is a solution of the basic equations when constitutive laws are taken into account, for which the Clausius Duhem inequality holds. For instance, for simple materials, the (c.u.) are w, s, σ, q ($w = e - T s$ is the free energy) and are expressed as functionals:

$$C = \underset{t' \leq t}{\mathfrak{F}} \left\{ F(\hat{x}_\alpha, t), \quad T(\hat{x}_\alpha, t'), \quad g(\hat{x}_\alpha, t'); \quad \hat{x}_\alpha \right\} \qquad (19)$$

where $g = \nabla T$. In order to discover the restrictions imposed on admissible processes, the expressions (19) are introduced in (18). Assuming that the F 's are Frechet-differentiable, that their arguments F, T, and g have time derivatives (at least right derivatives) and noting that, at each t, the values of these derivatives may be chosen independently, one shows that the coefficients of these derivatives in the right-hand side of (18) must be zero. This analysis provides the necessary and sufficient conditions for a process to be admissible.

We must content ourselves here with this general outline which has been applied successfully with care and rigor to various cases. General properties have been proved and classical thermostatics results recovered by an asymptotic analysis. Such rigorous achievements must be put on the credit side of this well-founded mathematical theory.

2 The Entropy Balance Assumptions.

Following Müller [7, 8] one may assume only that s—but not T—is a primitive quantity which fulfills a balance equation like (7) with $B = s$, $B^* = \sigma^*$. More precisely one assumes that

(*a*) the rate of entropy production σ^* is non-negative for admissible thermodynamical processes;

(*b*) the associated entropic flux j_s, like s, is a constitutive quantity;

(*c*) the supply φ_s is linear with respect to the other supplies with coefficients that are constitutive quantities;

(*d*) the normal component of the entropy flux across a surface of discontinuity Σ satisfies a conventional continuity requirement. For instance, if [.] denotes the jump of a quantity and if the system is at rest [$j_s \cdot \mathbf{n}$] = 0 if [θ] = 0.

From these quite natural assumptions, it is possible to prove in many cases the existence of the absolute temperature, to find the precise expression of j_s and φ_s as well as the restrictions on the constitutive equations.

The method to derive these results implies two steps. The first step is to write that the entropy production σ^* cannot be negative for fields constrained by the condition that they are solutions of the basic equation. Liu has shown that one can get rid of these constraints by the use of Lagrange multipliers which are new unknown constitutive quantities[7]. One then gets an expression for σ^* which must be non-negative whatever by the (p.u.). Taking account now of the assumed constitutive equations, the expression of σ^* involves linearly a number of derivatives of the constitutive variables, whose coefficients must vanish, because at each t the values of these derivatives may be chosen independently. The second step is to use the preceding condition (*d*) which allows one to exhibit the universal character of some quantities and their physical significance by looking at the simple case of equilibrium.

We must refer to the literature for the details of this rigorous and quite interesting method; we will only comment on some applications.

In thermoelasticity [9] the application of the first step leads to:

$$\dot{s} = \Lambda(\theta)[\dot{e} - \rho^{-1} \, tr \, \{t \cdot \dot{L}\}],$$

$$j_s = \Lambda(\theta)q, \quad \frac{d\Lambda}{d\theta} q \cdot \nabla\theta \geq 0;$$

here $\Lambda(\theta)$ is the only Lagrange multiplier which is not zero. The second step leads to the conclusion that Λ is a *universal function* which is easily identified with T^{-1}. All the classical results are recovered.

An instructive application concerns a mixture of inviscid fluids. *The analysis and the results depend on the basic equations chosen* (see I.2). If one takes (11), it is convenient to choose as constitutive quantities:

$$e_I, \, \sigma^\lambda = -p^\lambda, \, q_I, \, m_I^\lambda = m^\lambda - \tau^\lambda v$$

instead of (16), with "intrinsic" integral energy e_I and heat flux q_I defined by:

$$\rho \, e_I = \sum_{\lambda=1}^{\nu} \rho^\lambda e^\lambda, \quad q_I = q - \sum_{\lambda=1}^{\nu} \frac{1}{2} \rho^\lambda \, (u^\lambda)^2 \, u^\lambda.$$

After the first step, one gets the equation that gives $\rho \, ds$ in terms of $d(\rho \, e_I)$ and $d \rho^\lambda$ and the equations that give the entropy flux j_s in terms of q and u^λ as well as the supplies φ_s in terms of f^λ and r. But, Lagrange multipliers remain in the coefficients of these equation. Now the second step, when condition (*d*) is conveniently formulated for an impermeable or semipermeable wall for a constituent shows that, again, the multiplier of the energy equation may be identified with T^{-1}, and that another quantity has to be continuous for each fluid, a result that leads to the introduction of the chemical potentials μ_I^λ. Let us write some of the results:

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[7] In most cases, it may be proved that they do not depend on the supplies.

$$d(\rho e_I) = T d(\rho s) + \sum_{\rho=1}^{\nu} \mu_I^\lambda d \rho^\lambda,$$

$$\rho(e_I - Ts) = \sum_{\rho=1}^{\nu} \rho^\lambda \mu_I^\lambda - p$$

$$(20)$$

$$T j_s = q_I - \sum_{\lambda=1}^{\nu} \rho^\lambda \mu_I^\lambda u^\lambda,$$

$$T \varphi_s = r - \sum_{\lambda=1}^{\nu} \rho^\lambda u^\lambda \cdot f^\lambda, \quad p = \sum_{\lambda=1}^{\nu} p^\lambda$$

These results are very remarkable: Gibbs equation for the mixture $(20)_1$ and Gibbs-Duhem equation $(20)_2$ have been proved, correct expressions for j_s and φ_s have been found. In the residual inequalities appear all the dissipative mechanisms producing entropy: heat conduction, chemical reactions, momentum, and thermal diffusion. This is the starting point of a complete "rational thermodynamics" of fluid mixtures developed by Müller.

A last example, again due to Müller [10], concerns a single inviscid fluid whose constitutive equations depend on the constitutive variables $\rho, \theta, \dot{\theta}, \nabla \theta$. It is found that:

$$j_s = \Lambda(\theta, \dot{\theta}) q, \quad \varphi_s = \Lambda(\theta, \dot{\theta}) r.$$

Moreover $\Lambda(\theta, \dot{\theta})$ is a *universal function*, the *coldness*, whose equilibrium value reduces to $\Lambda(\theta, 0) = T^{-1}(\theta)$. This example is quite instructive: *the absolute temperature concept and the Gibbs equation in its classical form are only valid for equilibrium.*

3 A Challenge to Mathematicians? What we have called the "first" rational thermodynamics considers entropy and absolute temperature as primitive concepts. With Müller, only entropy was assumed, and it was proved in many interesting cases that an absolute temperature may be defined. The last step would be to justify the existence of both concepts on the basis of a statement comparable to the Caratheodory "inaccessibility" axiom for thermostatics. Müller has again considered the question in the frame of thermoelasticity and gave a precise formulation of the challenge: roughly speaking one has to find a statement that ensures the existence of certain quantities (entropy flux and supply, Lagrange multiplier) such that a precise inequality holds for any solution of the equations of motion [9].

4 Alternative Versions of Rational Thermodynamics. Recent attempts to develop further the axiomatic basis of thermodynamics must be mentioned [11], although it is impossible to give them the developments they deserve.

The basic ingredients are the concepts of "state" and "process," like in the Noll's new conception of continuum mechanics. Each process P associates to a state σ one another state $P\sigma$ and to each pair of processes corresponds, when it can be defined, the resulting process of the pair. For the statement of the laws of thermodynamics, the concept of an "action" $a(P, \sigma)$ is introduced in order to render precise and general the idea of "an integral along a process." It assigns to each pair (P, σ) a number (the supply of a in going from σ to $P\sigma$) with the requirements of continuity with respect to σ and additivity with respect to resulting processes. An action has the *conservation property* (alternatively *Clausius property*) at σ, if for every "nearly cyclic" process P starting at σ (and arriving inside an η-neighborhood of σ): $|a(P, \sigma)| < \eta$ or $a(P, \sigma) < \eta$. In any branch of thermodynamics, one must introduce an action $\hat{\epsilon}$ which has the conservation property for at least one state (first law) and an action $\hat{s}$ which has the

Clausius property for at least one state (second law). That provides us with a quite reduced requirement. But in fact it may be proved (on some natural assumptions) that $\hat{\epsilon}(P, \sigma)$ has a potential $e(\sigma)$ and that $\hat{s}(P, \sigma)$ has an "upper potential" $s(\sigma)$. Of course $e(\sigma)$ is the internal energy and $s(\sigma)$ the entropy.

This abstract frame must be fitted in each branch of continuum mechanics by prescribing how a state and a process are defined by giving some constitutive functions of the state and by introducing the two actions $\hat{\epsilon}$ and $\hat{s}$. For instance, for an elastic element, σ is defined by a triplet, essentially the present values of the deformation gradient, of the internal energy and of the temperature gradient. The constitutive functions are the temperature, the stress tensor, and the heat flux vector. The processes are defined by the functions of time that appear in equations ruling the derivatives of the triplet—for instance div $j_Q + \varphi_Q$ in (3) *which is here considered as a part of the definition of the process.* For an element with fading memory, a state is defined by the previous triplet *and* by their past history up to, but not including, the present time. This new thermodynamics is also able to include the theory of plasticity [12]. It appears then as a method for reorganizing the results of a given theory into a unified and rigorous scheme which permits us to derive general properties and the thermodynamical restrictions on response functions, more than a guide to discover a convenient schematization in a new field.

A recent paper [13] leads to a definition of the action $\hat{s}$ which is more closely related to the earlier considerations of Clausius, Kelvin, and Planck. It provides us with a new and interesting way to introduce absolute temperature and entropy in thermodynamics.

III The Local Accompanying State Model (l.a.s.)

The model described in the following is in essence very well known and is developed and commented on in various books [14, 15] and papers [16], most of them dealing with the so-called thermodynamics of irreversible processes (TIP). Nevertheless, its mathematical and physical consistency has been recently largely improved; it is then worthwhile to recall quickly some of its main features.

1 Internal Variables, Thermodynamical Potential, and Equations of State. As was mentioned in *II*.1, reversible processes in thermostatics correspond to a time scale such that the internal energy and the deformation variables are adequate to define at each time the state of the system, and these variables may be independently controlled by the observer. If the time of evolution one wants to consider is shorter, it is often possible to extend the previous space into a larger one in which processes can be described by the classical methods of thermostatics. The additional variables that have to be introduced, the *internal variables*, characterize quite generally *dissipative mechanisms*; they may change without changes in the surroundings, and usually the observer is not able to control their value.

Let us present, somewhat formally, how the model works. Having in mind a continuum, one uses quantities defined on each particle: specific internal energy e, variables that describe the deformation in the adopted—possibly generalized [5]—kinematical description $\chi = (\chi_1, \ldots, \chi_n)$, internal variables[8] $\alpha = (\alpha_1, \ldots, \alpha_p)$. The main assumption is that one may attach to any particle a thermostatic system (of unit mass) defined by (e, χ, α), which is significant for the physical description of the particle. For this "accompanying" system, the Gibbs equation may be written:

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[8] One does not specify here the tensorial character of the χ and of the α. For simplicity they will be considered as scalars.

$$T^a \, ds^a = d \, e - \sum_{i=1}^{n} \eta_i^a d \, \chi_i + \sum_{k=1}^{p} A_k^a d \, \alpha_k \qquad (21)$$

Generally, the superscript a will be omitted: then $T = T^a$, $s = s^a$ are, respectively, an absolute temperature and a specific entropy which may be used for the description of the particle. The conditions under which such an interpretation may be physically reasonable will be discussed in the following.

Then if one writes $e(s, \chi, \alpha)$ the specific internal energy (alternatively $w(T, \chi, \alpha)$ the specific free energy), one may express T, η, A (alternatively s, χ, A) as functions of s, χ, α (alternatively T, χ, α). These equations are the *equations of state* of the material. *Generally*, in account of the thermodynamic stability requirements, $e(s, \chi, \alpha) = e(\tilde{\chi})$ is a convex lower semicontinuous function of its arguments; one says also a *convex closed* function in order to recall that the epigraph of e (i.e., the domain $z \geq e(\tilde{\chi})$ in the space $\tilde{\chi}, z$) is a convex closed set. Then one may apply all the concepts introduced in convex analysis [4]. The dual function $e^*(T, \eta, -A) = e^*(\tilde{\eta})$ of e, obtained by a *Legendre-Fenchel transformation*, may be used in order to write the equations of state in an equivalent way; subgradients may be introduced if e or e^* are not differentiable. With the notation:

$$(\tilde{\chi}, \tilde{\eta}) = T \, s + \sum_{i=1}^{n} \eta_i \chi_i + \sum_{k=1}^{p} (-A_k) \alpha_k \qquad (22)$$

one may say that $\tilde{\chi}$, $\tilde{\eta}$ are connected by the equations of state if one of the following three equivalent statements holds:

$$e(\tilde{\chi}) + e^*(\tilde{\eta}) - (\tilde{\chi}, \tilde{\eta}) = 0, \quad \tilde{\eta} \in \partial \, e(\tilde{\chi}), \quad \tilde{\chi} \in \partial \, e^*(\tilde{\eta}) \qquad (23)$$

By definition, if the left-hand side of $(23)_1$ is not zero, it is positive. Other thermodynamical potentials, i.e., functions from which the equations of state may be written with gradients (or subgradients), may be built from $e(\tilde{\chi})$ by a *partial Legendre-Fenchel transformation*; that is precisely the case for the specific free energy.

2 Production Rate of Entropy and Dissipation. Complementary Constitutive Equations.

Let us assume, as usual in classical continuum mechanics, that the entropy balance equation can be written with $T \, j_s = q$, $T \, \varphi_s = r$, i.e., that Clausius Duhem inequality (18) holds. From (21) one may write:

$$\left.\begin{aligned} \dot{e} &= \rho \, T \, \dot{s} + \epsilon_{(i)}^r \, ; \\[2mm] \epsilon_{(i)}^r &= \sum_{i=1}^{\eta} \eta_i \, \tilde{\chi}_i - \sum_{k=1}^{p} A_k \dot{\alpha}_k = (\eta, \dot{\chi}) - (A, \dot{\alpha}) \end{aligned}\right\} \qquad (24)$$

Then (18) may be written:

$$\epsilon_{(i)} - \epsilon_{(i)}^r - q \, . \, \nabla \, (\text{Log } T) = \rho \, T \, \sigma^* = d \qquad (25)$$

One calls d the *dissipation* (per unit volume), $d_1 = \epsilon_{(i)} - \epsilon_{(i)}^r$ the *intrinsic dissipation*, $d_2 = d - d_1$ the *thermal dissipation*. By construction $\epsilon_{(i)}$, the opposite of internal power in the *real* evolution, involves the (generalized) strain rates which appear in the chosen kinematical description. One may prove in most cases that they may be chosen as derivatives of generalized strains (as for instance in (6)) and we may assume that the χ_i introduced in the foregoing are precisely the (generalized) strains. As a consequence $\epsilon_{(i)}^r$ which is analogous to $\epsilon_{(i)}$ in the associated artificial reversible evolution of the accompanying state is, like $\epsilon_{(i)}$, linear in the $\dot{\chi}_i$. Consequently (25) may be written:

$$d = (\eta^{an}, \dot{\chi}) + (A, \dot{\alpha}) - q \, . \, \nabla(\text{Log } T) \qquad (26)$$

Then d has the familiar expression,

$$d = \sum_{\mu=1}^{m} Y_\mu X_\mu = (Y, X) \qquad (27)$$

where the Y_μ stand for the "fluxes" ($\dot{\chi}$, $\dot{\alpha}$, q) an X_μ for the "forces" (η^{an}, A, $-\nabla(\text{Log } T)$).

Going back to *I.3*, it is easily recognized that in the l.a.s. model *the constitutive equations are given by the equations of state and by the complementary constitutive equations which express for instance the η^{an}, $\dot{\alpha}$ and q in terms of $\dot{\chi}$, A, and $\nabla(\text{Log } T)$ or more generally, which relate the Y and the X.*

When the preceding classical assumptions for j_s and φ_s are not valid, the crucial point is to first derive the convenient expressions for these quantities, and consequently for the dissipation d, in a way which is consistent with the chosen basic equations. In each case, ad-hoc methods, which rest on physical reasoning, are adopted; one then must be careful to fulfill the consistency requirements, for instance to exclude the outside supplies from the expression of d. In some cases, as said before (*II.2*), the analysis of Müller provides a systematic method to answer these questions. The next three subsections are devoted to the formulation of the complementary equations (c.c.e.).

3 Classical Model of TIP.

TIP originated from the decisive contributions of Onsager and Casimir and is presented in many books authored by Meixner and Reik, Prigogine, de Groot and Mazur [14], Woods [3], and many others. Quite interesting, stimulating and also critical discussions may be found in [10] about the statistical foundations, the various branches of physics where it may be applied, and the impressive set of experiments that support the validity of the Onsager-Casimir reciprocity relations (OCRR) which is the basic tool of TIP. These relations say that, when the "fluxes" Y and the "forces" X are linearly related, the c.c.e. may be written:

$$X_i = \sum_{j=1}^{M} L_{ij} \, Y_j \qquad (28)$$

where the matrix L_{ij} is *symmetric, non-negative*[9] and may depend on the thermodynamical variables, and especially on T and χ_i. Other restrictions arise from the tensorial character of the Y and the X, the frame invariance and the material symmetry.

Such a result requires a proper choice between the Y and the X in the right-hand side of (27). In a specific situation ad-hoc considerations give the answer and no difficulty arises. For instance, strain rates, heat flux vector, and rates of progress of chemical reactions have to be listed among the Y. A rigorous recipe [3] may be given if one accepts to introduce the concept of a "microscopic time reversal" (mtr) for which $Y \to -Y$, $X \to +X$ (it corresponds to a time interval smaller than the collision time). One can write (28) if the linearly related Y and X have a definite parity under mtr. Conjugate linear transformations $Y \to Y'$, $X \to X'$ may be applied, provided $(Y', X') = (Y, X)$. The OCRR may also be generalized when the Y and the X are not dependent but satisfy some linear constraints [17].

4 The Pseudopotential of Dissipation Model or Standard Model.

In TIP, one may write (28)

$$X_i = \frac{\partial \varphi}{\partial Y_i}, \quad \varphi = \frac{1}{2} \sum_{i=1}^{m} \sum_{j=1}^{m} L_{ij} \, Y_i \, Y_j \qquad (29)$$

where $\varphi(Y)$ is a quadratic non-negative form. *The standard model presented now is a generalization of (29), when $\varphi(Y)$ is assumed to be a non-negative convex closed function such that $\varphi(0) = 0$.*

This assumption leads to thermodynamical admissible process because d is consequently non-negative. This pseudopotential (p.p.) $\varphi(Y)$ may, in some cases, depend on

---

[9] Then d is necessarily non-negative.

the thermodynamical variables that have to be considered as parameters.

Needless to say, other p.p. may be introduced, as mentioned for the thermodynamical potentials in *III*.1, by a complete Legendre-Fenchel transformation which leads to $\varphi^*(X)$, again a convex closed p.p., or by a partial Legendre-Fenchel transformation which leads to a saddle (convex-concave) p.p.. General formulations of the c.c.e. may be written in a similar way to those in (23) given for the equations of state. In conclusions, for such a model, all *the constitutive equations of the material can be recast in two non-negative convex closed functions, the potential e and the pseudopotential φ.*

The present formulation is essentially due to Moreau [18], see also [4, 19]. It is impossible here to give an account of all the contributions which have been useful to prepare this formulation. Plasticity theory, with its normality rule, played an important role in order to focus attention on the importance of convexity. A decisive step must be attributed to Ziegler [20] when he recognized the role of "dissipation functions."

5 General Formulation of c.c.e. Although the p.p. model can be used to describe a great variety of physical situations, it does not possess a universal validity. Quite a general formulation may be proposed by assuming that the X and Y are functionally related with, possibly, the thermodynamical variables as parameters. For instance, for a dissipation like (26)

$$\eta^{an}, \ \dot{\alpha}, \ q = \mathfrak{F} \ (\dot{\chi}, A, \ \nabla \ (\text{Log } T); \ T, \chi, \alpha) \qquad (30)$$

The function $\mathfrak{F}$ must satisfy the causality, the objectivity and the material symmetry requirements, and must also lead to a solution of the basic equations, supplemented by (30) and the equations of state, for which d is never negative, a condition that was automatically fulfilled in the standard model.

6 Physical Significance of the l.a.s. Model. It is already known that any rheological model composed of springs, dashpots, and gliders is a standard model [21]. Considerations on rheological models throw some light on the understanding of two important questions concerning the l.a.s. method: what is the significance of the thermodynamic potential e? How is it possible to select the internal variables α?

In order to simplify, one will assume that the χ variables reduce to ϵ, strain tensor in small perturbation theory, and that the system has only elastic stresses ($\eta = \sigma$, $\eta^{an} = 0$). In essence, the l.a.s. method assumes that a particle in the usual macroscopic description (M.D.) represents in fact a microscopic structure or cell which is itself a continuum in the microscopic description (m.d.). Then e, local value in M.D., can be looked upon as the *global* internal energy of the corresponding cell in m.d. (per unit mass). Similarly ϵ, local strain in M.D., can be looked upon as the *global* geometrical description of the cell. Keeping e and ϵ constant means that the cell, from a thermodynamical point of view, is isolated. This cell may be highly heterogeneous and various physical dissipative mechanisms may be involved in the evolution, each of them being described by an internal variable α. If one wants to keep only a finite number of α, one must take into consideration the characteristic time of the macroscopic evolution, i.e., of the macroscopic strain rates, say $\tau_M = \epsilon \cdot \dot{\epsilon}^{-1}$, and the characteristic value of the bound of macroscopic stresses, say σ_M. The dissipative mechanisms characterized by a relaxation time (like for viscosity) of the same order than τ_M must be kept. The rate-independent mechanisms (like for plasticity) whose yield limits are below σ_M must be kept. If one α has a relaxation time much greater than τ_M or a yield limit much greater than σ_M, its value is considered as frozen and it plays no role in the l.a.s. method. The α which have relaxation times much shorter than τ_M do

not appear either because they are considered to have the equilibrium values, they reach, when *the whole system has been considered isolated with e, ϵ, and all the others α frozen.* Then, the definition of the system associated with a particle, i.e., the choice of the $\alpha_1 \ldots \alpha_p$ depends on the degree of the refinement which seems suitable; it is not a well-defined entity. *Consequently T^a, s^a, η_i^a, A_k^a in (21) depend on the choice of the α which have been kept.* In particular, in the l.a.s. model, absolute temperature and specific entropy are not uniquely defined and have only a relative significance. When one writes $T = T^a$ and $s = s^a$ as was done in the foregoing, one assumes that these ad-hoc definitions may correctly represent what may be called temperature[10] and entropy in a system in motion, which is not in thermostatic equilibrium [16].

7 Comparison and Connection With the Models of Rational Thermodynamics. In such a comparison with the l.a.s. models, the models of rational thermodynamics present some points of superiority from the point of view of rigor while the l.a.s. method seems to be more efficient. Rational thermodynamics does not assume the validity of Gibb's equation which becomes a theorem; such an assumption is essential in any l.a.s. model, which consequently claims to be only valid for systems *near equilibrium*. Rational thermodynamics must start with specific classes of material whose constitutive equations obey precise requirements; an l.a.s. model prefers, as it is traditional in classical thermodynamics, to leave things more open, and to start only with the thermodynamical description of the l.a.s. which may be used for quite different dissipative mechanisms. But in a specific field—say for instance viscoelasticity or mixture of fluids—final results are quite comparable, when internal parameters have been, formally at least, eliminated, although those deriving from rational thermodynamics are usually more general [16].

But the flexibility of the l.a.s. method is probably its main advantage along with the simplicity of the formulation of the constitutive equations, especially for standard materials. It may be adapted to many field of application; it remains open to further improvements of its physical significance and of its mathematical consistency. It provides constitutive laws simple enough to allow for quite interesting mathematical studies and numerical analysis of the mechanical systems to which it may be applied. These points which have been described in the foregoing as *main objectives* of continuum thermodynamics will be briefly illustrated in the following sections.

IV Applications

The present section is restricted to four examples related to isothermal solid mechanics in the frame of small perturbation theory[11]. The thermal dissipation is neglected. When it is not, if intrinsic and thermal dissipation are uncoupled, the generalized Fourier's law for a standard model is:

$$q = -\frac{\partial \varphi_{th}}{\partial \xi}, \quad \xi = \nabla \ (\text{Log } T) \qquad (31)$$

where $\varphi_{th} (\xi)$ is a convex non-negative function with $\varphi_{th}(0) = 0$. It reduces to the usual Fourier law for small deviations from a fixed T_0. One will deal also only with materials with *elastic stresses* ($\sigma^{an} = 0$).

1 Plasticity With Hardening. The internal variables α and their conjugates A will be chosen as:

$$\alpha = (\epsilon^p, \ \beta, \ p), \quad A = (\sigma, \ B, \ R) \qquad (32)$$

---

[10] Other choices are possible in the frame of the l.a.s. model. For instance, Meixner assumes that $s = s^a$ but $T \neq T^a$, [10].

[11] For application to finite-deformation theory of plasticity, see Mandel's paper "Thermodynamics and Plasticity" in [10]. See also Sidoroff [17].

and the free energy will be written:

$$\rho \, w = \frac{1}{2} \, (\epsilon - \epsilon^p) a (\epsilon - \epsilon^p) + k(\beta) + h(p) \qquad (33)$$

Here, a is a fourth-order tensor (a_{ijlm}), ϵ^p the plastic strain, β and p, respectively, a tensorial (symmetric) and a scalar parameter that describe the hardening effect, $k(\beta)$ and $h(p)$ two scalar-valued functions. The equations of state are:

$$\sigma = a(\epsilon - \epsilon^p), \quad B = -\frac{dk}{d\beta} = -k'(\beta),$$

$$R = -\frac{dh}{dp} = -h'(p) \qquad (34)$$

and the dissipation is:

$$d = (\sigma, \dot{\epsilon}^p) + (B, \dot{\beta}) + (R, \dot{p}) \qquad (35)$$

In the A space, a convex domain P is introduced, with K_0 a constant:

$$P : J(\sigma + B) + R - K_0 \leq 0, J(\tau) = \sqrt{\tau_{ij}^D \, \tau_{ij}^D} \qquad (36)$$

with τ^D the deviatoric part of τ. The c.c.e. are defined by the p.p. $\varphi^*(A)$:

$$\varphi^* = I_p(A) \qquad (37)$$

with I_P the indicator function of P, i.e., the (generalized) closed convex function which is zero in P and $+\infty$ outside P. The c.c.e. may then be written:

$$\dot{\epsilon}^p = \dot{\beta} = \lambda \frac{\sigma^D + B^D}{J(\sigma + B)}, \quad \dot{p} = \lambda \; (\lambda \geq 0) \qquad (38)$$

It is easily seen that β may be identified with ϵ^p, and p with the cumulated plastic strain since:

$$\dot{p} = \sqrt{\dot{\epsilon}^p \dot{\epsilon}^p} \qquad (39)$$

If $k(\beta)$ is a constant, one gets the model of isotropic hardening: the domain P of elasticity keeps a constant center, but its size is modified with the evolution. If $R(p)$ is a constant, one gets a model of *kinematic hardening*: the size and the shape of P remain unchanged, but its center may move with the evolution; linear kinematic hardening (Prager) is obtained with a quadratic $k(\beta)$.

2 Viscoplasticity. A class of rate-dependent viscoplastic materials may be defined by the previous formulas (32)–(36), with a p.p. $\varphi^*(A)$ of the Norton-Hoff type (Friaa [22]):

$$(n+1) \, \varphi^*(A) = \mu \left\{ j_p(A) \right\}^{n+1} \qquad (40)$$

where j_p is the gauge function of the convex domain P, for instance to be specific, the domain defined by (36). Again, β may be identified with ϵ^p, equation (39) holds and:

$$\dot{\epsilon}^p = \frac{\mu}{K_0} \left(\frac{J(\sigma + B) + R}{K_0} \right)^n \frac{\sigma^D + B^D}{J(\sigma + B)} \qquad (41)$$

The previous result (38) is recovered for $n \to +\infty$.

3 Cyclic Plasticity. Experimental data show that the previous model (41) is not satisfactory for cyclic loadings. Chaboche [23] obtained a good agreement with experiments with a suitable modification. Instead of (40), let us take a p.p. which will depend on the thermodynamical variables:

$$\varphi^*(A; \alpha) = \frac{\mu}{n+1}$$

$$\times \left\{ \frac{2(J(+B) + R) + \eta[(B,B) - (k'(\beta), k'(\beta))]}{K_0} \right\}^{n+1} \qquad (42)$$

The term added in the right-hand side of (42) vanishes in a real evolution according to (34). Previous (38), (39), and (41) are still valid but now:

$$\dot{\beta} = \dot{\epsilon}^p + \eta \, B \, \dot{p} \qquad (43)$$

The new term in the right-hand side of (43) is precisely the term introduced in Chaboche's theory which allows it to fit the experimental data.

4 Damage of Ductile Materials. Ductile fracture in metals involve considerable damage at crack tips, via nucleation and growth of voids initiated by inclusions. For the sake of simplicity, damage and hardening will be assumed isotropic and described by two scalar-valued variables D and p. Then, one takes:

$$\alpha = (\epsilon^p, D, p), \quad A = (\sigma, Y, R) \qquad (44)$$

and for the free energy, a suitable modification of (33)

$$\rho \, w = \frac{1}{2} \, (\epsilon - \epsilon^p) a (\epsilon - \epsilon^p) + m(D) + h(p) \qquad (45)$$

One will take a p.p. $\varphi^*(A)$ associated to a domain P which depends on the mean stress (J defined by (36)):

$$P : J(\sigma) + R + Y g(\sigma_m) \leq 0, \; 3 \, \sigma_m = tr\{\sigma\} \qquad (46)$$

If $\dot{\epsilon}^p$ and $\dot{\epsilon}^{pD}$ are the mean part and the deviatoric part of the plastic strain rate $\dot{\epsilon}^p$, then the c.c.e. may be written:

$$\dot{\epsilon}^p D = \lambda \frac{\sigma^D}{J(\sigma)}, \dot{\epsilon}_m^p = \lambda \, Y g'(\sigma_m), \quad \dot{D} = g(\sigma_m), \quad \dot{p} = \lambda \qquad (47)$$

Following Rousselier [24], one can derive the form of $g(\sigma_m)$, if one assumes first that D is related to the volume fraction of the growing microscopic voids, (i.e., D is a function of ρ) second that change of volume due to elastic strains may be neglected in the equation of continuity, i.e., $\dot{\rho} + 3 \, \rho \dot{\epsilon}_m^p = 0$. Then, according to (47):

$$g(\sigma_m) g'^{-1}(\sigma_m) = -3 \, \rho \, Y D'(\rho) \qquad (48)$$

But $Y = -m'(D)$ is also a function of ρ, and both sides have to be assumed to equal a constant. Looking at (47)$_2$ *the rate of extension of the damage is proportional to the exponential of triaxiality*. That is the result obtained by Rice-Tracey through a direct investigation of growth of cavities in ductile metals submitted to high stress triaxiality.

V Global Analysis in Continuum Thermodynamics

So far one has considered the thermodynamical description of the particle or of the "microscopic" cell which is schematized by this particle. One will now consider what are the thermodynamical concepts which have to be used for a system, like a structure. The present section shows that one *must* in some cases introduce some global variables, and that this introduction is quite useful, if not necessary, for a thermodynamical description of a structure.

Geometrically, Ω is the bounded domain of the structure in the x_i space[12], $\partial\Omega$ its boundary. The material is assumed to have elastic stresses ($\sigma^{an} = 0$). Evolutions are sufficiently slow to be quasi-static. Body forces are neglected; given loads [F^d per unit area] are applied on the part $\partial\Omega_F$, and displacements [u^d] are imposed on the complementary part $\partial\Omega_u$. Small perturbations are assumed. The system is assumed to be thermally isolated.

1 A First Example From Fracture Mechanics. Let us consider the propagation of a linear crack of length $l(t)$ in a solid undergoing two-dimensional deformation (plane strain, plain stress, antiplane shear). Assuming no surface contribution to energy or entropy on the crack, then the internal energy $E(\Omega)$ of the system is:

$$E = \int_\Omega \rho e \, d\Omega \qquad (49)$$

---

[12] The x_i are orthonormal coordinates; a comma is used for a partial derivative.

The energy balance leads to a quantity H which represents the heat source produced at the crack tip of the moving crack [25]: if Γ denotes a closed curve surrounding the crack tip and n the external normal, one obtains:

$$
\left.
\begin{aligned}
H &= \lim_{\Gamma \to 0} \int_\Gamma q \cdot n \, d\Gamma = J_0 \, \dot{l}_0 \\[2mm]
J_0 &= \lim_{\Gamma \to 0} \int_\Gamma (\rho \, e \, n_1 - n \cdot \sigma \cdot u_{,1}) \, d\Gamma;
\end{aligned}
\right\}
\qquad (50)
$$

The quantity J_0 appears as a crack tip force due to thermomechanical singularities at A. The heat source H appears in the expression of σ^* (through the term $T_A^{-1}H$) and then this source is a hot one. Moreover in the dissipation d, appears the term $J_0 \, \dot{l}$. One may get a model of the propagation law of the crack, by giving a p.p. $\varphi^*(J_0)$:

$$
\dot{l} \in \partial \, \varphi^*(J_0) \qquad (51)
$$

Griffith's criterion corresponds quite clearly to $\varphi^*(J_0) = I_\gamma(J_0)$, where I_γ is the indicator function of the convex domain $J_0 \le \gamma$.

This example shows that introduction of the global variable l and of the global function E may be quite useful.

2 Global Variables and Global Potentials. If one wants to introduce a global thermodynamical *potential* for the structure, one is led to consider *fields* of local variables as new global variables; such a field is then usually defined by a density in a volume, on a surface or along a line and will be denoted by a bold letter. The evolutions are assumed to be isothermal.

If the fields $\mathbf{F}^d$, $\mathbf{u}^d$, $\boldsymbol{\alpha}$ are given, the stresses and strains in Ω may be found by solving a problem of equilibrium as in elasticity. For instance the displacement field $\mathbf{u}$ is the kinematically admissible field $\mathbf{u}'$ for which:

$$
W'(\mathbf{u}':\mathbf{F}^d, \mathbf{u}^d, \boldsymbol{\alpha}) = \int_\Omega \rho \, w(\epsilon(u'), \, \alpha) \, d\Omega - \int_{\partial\Omega_F} F^d \cdot u' \, da \qquad (52)
$$

reaches its minimum value. The value of this minimum is by definition the *thermodynamical potential* for the variables $\mathbf{F}^d$, $\mathbf{u}^d$, $\boldsymbol{\alpha}$:

$$
W(\mathbf{F}^d, \mathbf{u}^d, \boldsymbol{\alpha}) \qquad (53)
$$

It is possible to prove that:

$$
\frac{dW}{dt} = \int_\Omega -A \cdot \dot{\alpha} \, d\Omega + \int_{\partial\Omega} (u \cdot \dot{F}^d + \sigma \cdot n \cdot \dot{u}^d) \, da
$$

in such a way that $\mathbf{A}$, the conjugate variable of $\boldsymbol{\alpha}$, is effectively the field of A in Ω. Moreover the conjugate variable of $\mathbf{F}^d$ is the displacement field on $\partial\Omega_F$, and the conjugate field of $\mathbf{u}^d$ is the field of traction $\sigma \cdot n$ on $\partial\Omega_d$. The analysis of the dissipation leads to a similar result and, for instance, in the example of $II.4$ related to damage mechanics one may write:

$$
d = \mathbf{A} \cdot \dot{\boldsymbol{\alpha}} = \int_\Omega ((\sigma, \dot{\epsilon}^p) + Y \dot{D} + R \, \dot{p}) \, d\Omega; \qquad (54)
$$

then σ, $\mathbf{Y}$, $\mathbf{R}$ may be considered as the variables conjugate (with respect to the dissipation) to the variables $\dot{\epsilon}^p$, $\dot{\mathbf{D}}$, $\dot{\mathbf{p}}$. For a standard material, a global p.p. may be introduced:

$$
\Phi(\dot{\boldsymbol{\alpha}}) = \int_\Omega \varphi(\dot{\alpha}) \, d\Omega, \quad \Phi^*(\mathbf{A}) = \int_\Omega \varphi^*(A) \, d\Omega \qquad (55)
$$

The introduction of global concepts is important not only to use a more compact notation but for many other reasons. A few of them may be mentioned:

1. In global potentials like (53) or (55) only the fields that are important for the analysis of the structure are kept;

2. It provides a quite useful framework to discuss physical

situations like friction, adhesion, unilateral contact, and elastically supported boundary (see for instance [26]);

3. It exhibits the consistency of thermodynamical concepts defined at the level of the particle with the thermodynamical concepts defined on the whole structure. This question will be considered again in Section VI.

If the evolutions are not assumed to be isothermal, the fields s and T have to be introduced

For instance, in the situation considered above in Section $V.1$, one may introduce, like in $V.2$, the potential of the structure of the field variables $\mathbf{F}^d$, $\mathbf{u}^d$, $\boldsymbol{\alpha}$, $\mathbf{s}$, and of l, say the global internal energy:

$$
E(\mathbf{F}^d, \mathbf{u}^d, \boldsymbol{\alpha}, \mathbf{s}, l) \qquad (56)
$$

It may then be proved [25] that J_0 defined by $(50)_2$ is also the conjugate variable of l for this potential:

$$
J_0 = -\frac{\partial E}{\partial l}(\mathbf{F}^d, \mathbf{u}^d, \boldsymbol{\alpha}, \mathbf{s}, l) \qquad (57)
$$

Then, as it is the case for internal variables, the thermomechanical force at the crack tip is at the same time the conjugate of l with respect to the thermodynamical potential, and the conjugate of l with respect to the dissipation, see (51) and (57).

The introduction of global variables is even more necessary when one deals with a three-dimensional crack extension: the crack front curve C is a global variable. In the thermodynamical analysis there appear the normal crack extension velocity field $\mathbf{V}$ along the curve C and its conjugate force density field $\mathbf{J}_0$ along the same curve.

VI Continuum Thermodynamics and Homogenization

The object of the present section is to bring more precisions to the considerations given previously in $III.6$. Homogenization refers to a method by which it is possible and reasonable, in an asymptotic sense, to substitute for a highly heterogeneous medium (at a microscopic level), a homogeneous continuum model (at the macroscopic level) [26, 27]. It will appear that some local variables in the macroscopic description are in fact related to global variables at the microscopic level.

To be specific, one will be concerned with materials that admit elastic stresses ($\sigma^{an} = 0$) and thermodynamic potentials, $e(\epsilon, \alpha, s)$, internal energy or $w(\epsilon, \alpha, \theta)$, free energy; θ is the absolute microscopic temperature. Then the equations of state may be written, for instance:

$$
\sigma = \rho \frac{\partial w}{\partial \epsilon}, \quad s = -\frac{\partial w}{\partial \theta}, \quad A = -\rho \frac{\partial w}{\partial \alpha} \qquad (58)
$$

Noting $\xi = \nabla(\text{Log } \theta)$, generalized Fourier's law (see $IV.1$) will be assumed:

$$
q = -k(\xi) \qquad (59)
$$

1 Preliminary Concepts and Notation. In the discussion of overall properties of heterogeneous media, it is essential to define a volume element that is small enough to allow us to distinguish the microscopic heterogeneities, yet large enough to represent the overall behavior of the heterogeneous medium. Such a volume element V is called the representative volume element (r.v.e.), (for periodic composite it is simply the elementary cell). Most of the macroscopic quantities (M.Q.) are the average on the r.v.e. of the microscopic quantities (m.q.), eventually extended in the case of holes or rigid inclusions. More precisely with ρ, σ, ϵ, e, w, s, ξ, q we associate $\bar{\rho}$, $\bar{\sigma}$, $\bar{\epsilon}$, $\bar{e}$, $\bar{w}$, $\bar{s}$, $\bar{\xi}$, $\bar{q}$ defined by:

$$\bar{\rho}=\langle\rho\rangle,\ \bar{\sigma}=\langle\sigma\rangle,\ \bar{\epsilon}=\langle\epsilon\rangle,\ \bar{q}=\langle q\rangle,\ \bar{\xi}=\langle\xi\rangle$$
$$\bar{\rho}\,\bar{s}=\langle\rho\,s\rangle,\ \bar{\rho}\,\bar{e}=\langle\rho\,e\rangle,\ \bar{\rho}\,\bar{w}=\langle\rho\,w\rangle \qquad (60)$$

where

$$\langle f\rangle=\frac{1}{|V|}\int_V f(y)\ dy \qquad (61)$$

y refers to the microscopic set of coordinates (local coordinates in the r.v.e. V), while x denotes the macroscopic coordinates.

Conversely, starting with the (M.Q.) $\bar{\sigma}$, $\bar{\epsilon}$, $\bar{q}$, $\bar{\xi}$, the definition of suitable corresponding (m.q.) σ, ϵ, q, ξ requires a *localization process*. Such a definition must obviously satisfy not only the corresponding conditions (60), but also the localization conditions. When a r.v.e. is chosen, suitable boundary conditions have to be prescribed. The set of boundary conditions must satisfy some requirements.

(*i*) It must allow us to define a *localization process*: any macroscopic state variables $\bar{\sigma}$, $\bar{\epsilon}$, $\bar{w}$, $\bar{\xi}$ being given, we must be able to find the m.q. σ, ϵ, w, ξ implied by the M.Q. ones, by mean of the microscopic constitutive laws, of the boundary conditions and of the equations of microscopic equilibrium:

$$\text{div}_y\ \sigma=0,\quad \text{div}_y\ q=0 \quad \text{(inertia effects on} \qquad (62)$$
$$\text{the microscale can be neglected).}$$

(*ii*) For mechanical reasons, Hill's macrohomogeneity condition must be fulfilled by all fields σ^*, ϵ^*, q^*, ξ^*:

$$\bar{\sigma}^*\bar{\epsilon}^*=\langle\sigma^*\epsilon^*\rangle,\quad \bar{q}^*\bar{\xi}^*=\langle q^*\xi^*\rangle \qquad (63)$$

As examples, let us mention [26].

(*1*) *Localization in Periodic* (*or Quasi-Periodic*) *Structure.* It is the theory of homogenization developed in some books [27] and in many papers, which appears to have numerous practical applications in various fields of mechanics. The cell V is such that by periodicity it generates the whole geometry (V is a special polyedron) and the boundary conditions on ∂V are simply that σ, ϵ, q, ξ take equal values on opposite sides of ∂V, a necessary condition resulting from the periodicity.

(*2*) *Hill-Mandel Stress-Flux Localization Process.* Boundary conditions on V are $\sigma\cdot n=\bar{\sigma}\cdot n$, $q\cdot n=\bar{q}\cdot n$.

(*3*) *Hill-Mandel Displacement-Temperature Localization Process.* The boundary conditions express that displacement u and $\log\theta$ are the traces on ∂V of linear functions of y in V, $u=\bar{\epsilon}\cdot y$, $\log\theta=\bar{\xi}\cdot y$.

A homogenization theory proceeds as follows: starting with the M.Q., using a localization process, knowing all the laws that connect the m.q., we get these quantities and we deduce the corresponding laws that connect the M.Q. This is the scheme that will be applied to thermodynamics in the following subsections.

2 Systems in Equilibrium (Thermostatics). One starts with $\bar{\epsilon}$, T, α where T is the temperature in the macroscopic description, and $\alpha(x,y)$ the field of internal variables will be considered as parameters. As a consequence of the equilibrium assumption, one will assume that T and θ may be practically equal (but not ∇T and $\nabla\theta$ because the latter may exhibit very high spatial oscillations due to the heterogeneities). It is possible to find σ, ϵ, q, ξ as functions of E, T, α, and $\bar{\xi}$ by solving in the cell V, the equations (62) supplemented by the conditions $(60)_3$ and $(60)_5$, the constitutive laws (58) and (59) and the localization boundary conditions. For a given localization process, this solution is unique. If then one computes $\bar{\sigma}$, $\bar{e}$, $\bar{s}$, $\bar{w}$, and $\bar{q}$ by (61), it may be *proved* that:

$$\bar{\sigma}=\bar{\rho}\frac{\partial\bar{w}}{\partial\bar{\epsilon}}\ (\bar{\epsilon},\ T,\ \alpha)=\bar{\rho}\frac{\partial\bar{e}}{\partial\bar{\epsilon}}\ (\bar{\epsilon},\ s,\ \alpha)$$
$$\bar{s}=-\frac{\partial\bar{w}}{\partial T},\quad T=\frac{\partial\bar{e}}{\partial\bar{s}} \qquad (64)$$

thus usual state laws are valid in the macroscopic description. Moreover (64) gives the stress-strain relation of the homogenized material, and similarly it is possible to find the generalized Fourier law for this material which gives $\bar{q}$ as a function of $\bar{\xi}$.

For instance, for a periodic structure whose constituents are linearly thermoelastic, the free energy may be written:

$$2\ \rho\ w(\epsilon,\ \theta)=(\epsilon-\lambda\theta)\ a(\epsilon-\lambda\theta)-(\lambda\ a\lambda)\ \theta^2-\beta\ \theta^2 \qquad (65)$$

where a is a fourth-order tensor, λ a second-order tensor, β a scalar, all of them being functions of x and y. It is then possible to prove that the homogenized body is itself thermoelastic and that $2\ \bar{\rho}\ \bar{w}(E,T)$ has an expression similar to the right-hand side of (65), with coefficients a^{hom}, λ^{hom}, β^{hom} functions of x only which may be uniquely computed with the mean value operator $<\ >$ when a finite number of boundary problems have been solved on the cell V.

3 Thermodynamical Evolutions Very Close to Equilibrium. The precise hypothesis is now that the characteristic time τ_M of the macroscopic evolution is large as compared to any time of propagation inside the cell.

If one admits that the first and second principles may be written with m.q.:

$$\rho\ \dot{e}-(\sigma,\ \dot{\epsilon})+\text{div}\ q=0,\ \rho\ \theta\ \dot{s}+\text{div}\ q-q.\xi\geq0$$

then it is possible to prove that the corresponding laws are still valid for the corresponding M.Q. and that at each time t equations (64) hold. This means that the thermostatic description and Gibb's equation are valid for the homogenized material, if they are assumed to be valid for the constituents.

4 Nonequilibrium Evolutions and Local Equilibrium State. If the temperature θ cannot be assumed to be nearly uniform in the cell V or if the characteristic time in the cell is of the same order as τ_M, the previous analysis fails. In particular, equations (62) are no longer valid since inertia effect with small wavelengths must be taken into account.

At each time t, one may apply to a cell the artificial process described in *III*.6 for which the cell is isolated. As was said in the foregoing, $\bar{e}$, $\bar{\epsilon}$, and some of the α have to be kept constant; those α, say α', which have relaxation time shorter than τ_M are functions of time t, like all the other quantities defined on the cell. One has to study a dynamical evolution toward equilibrium in order to get the m.q. that characterize this equilibrium. For instance, if the set of α' is empty, one has to study a dynamical thermoelastic evolution toward equilibrium. Then one gets the microscopic local accompanying state. The l.a.s. defined in *III*, and especially in *III*.6, is obtained when applying to this microscopic state the technique of homogenization like in *VII*.3.

The anaysis of this section is surely not a decisive justification of the model described in *III* and applied in *IV* and *V*. But it strengthens the interpretation given in *III*.6 and gives an interesting contribution to prove at least the consistency of the model and, simultaneously, a new example of the usefulness of the method of homogenization and localization in order to study highly heterogeneous media.

VII Bifurcation and Stability

In this last very brief section, we want to cite a few general results concerning the stability of the evolutions of systems of

standard materials (*III*.4). For the sake of simplicity one will assume that the thermal dissipation is negligible (adiabatic or isothermal evolutions).

1 Convexity and Stability. If the material is elastic (no dissipation), the solution of an equilibrium problem corresponds to the minimum of the deformation energy $W'(\mathbf{u}, \mathbf{F}^d, \mathbf{u}^d)$ on the set of the kinematically admissible displacements. On an equilibrium path, the first variation of W must be zero and it has been proved that if the second variation is positive, then the system is stable and no bifurcation is possible:

$$W'_{,\mathbf{u}^2}(\mathbf{u}, \mathbf{F}^d, \mathbf{u}^d).\delta\mathbf{u}^2 > 0 \tag{66}$$

Inequality (66) expresses the local and strict convexity of the thermodynamic potential on the equilibrium path. This theorem is also valid for finite deformation.

This known result may be generalized to most thermoelastic and viscoelastic systems. For example, the Kelvin-Voigt material [28]. *Joint, strict convexity of the thermodynamic potential and of the p.p. potential ensure in general the stability* of an equilibrium.

This result generalizes directly, but significantly, those of Prigogine and his coworkers who have emphasized in the frame of TIP [15] the importance of monotonicity of the force-flux relation:

$$(A_1(\dot{\alpha}_1) - A_2(\dot{\alpha}_2)).(\dot{\alpha}_1 - \dot{\alpha}_2) \ge 0 \tag{67}$$

which expresses simply the convexity of the p.p. potential $\varphi(\dot{\alpha})$.

2 Special Case of Systems for Which p.p. $\varphi^*(A)$ is the Indicator Function of a Convex Domain. As is well known and as was mentioned previously, such cases appear in plasticity theory and in brittle fracture mechanics. The p.p. $\varphi(\dot{\alpha})$ is a positively homogeneous function of degree 1 and $\varphi^*(A)$ is the indicator function I_p of a convex, closed domain P. As seen in Section *V*.2 or *V*.3, such a system has a global potential W and a global p.p. ϕ^*:

$$W = W(\mathbf{F}^d, \mathbf{u}^d, \alpha), \mathbf{A} = -\frac{\partial W}{\partial \alpha}, \phi^* = \phi^*(\mathbf{A}) \tag{68}$$

and the corresponding c.c.e.:

$$\dot{\alpha} \in \partial\phi^*(\mathbf{A}) \tag{69}$$

is equivalent to Hill's maximum dissipation, i.e., for any A^* in P:

$$(\mathbf{A} - \mathbf{A}^*).\dot{\alpha} \ge 0.$$

The evolution of the system is obtained by solving (68) and (69) with initial condition $\alpha(0)$.

Here again, the positivity of the second derivative $W_{,\alpha^2}$ plays an important role in bifurcation and stability analysis. Following Hill, by studying the incremental response when $\varphi(\dot{\alpha})$ does not depend on the actual state [29], one obtains:

$$\left.\begin{array}{l} W_{,\alpha^2} \text{ strictly positive on } \partial I_p(A) \Rightarrow \text{ stability} \\[2mm] W_{,\alpha^2} \text{ strictly positive on } \overline{\overline{\partial I_p}}(A) \Rightarrow \text{ nonbifurcation} \end{array}\right\} \tag{70}$$

where $\partial I_p(A)$ is the normal cone and $\overline{\overline{\partial I_p}}(A)$ the subspace generated by vectors of the normal cone.

These criteria have been applied successfully to various problems of solid mechanics: plastic buckling, stability of interacting cracks in brittle fracture, etc. . .

Conclusion

We have tried to exhibit some of the most significant lines of research which have appeared in literature during the last 15–20 years in the field of continuum thermodynamics. Nevertheless, continuum thermodynamics is still in the process of full expansion. Progress may be expected in the next few years in many directions: the improvement of the formulation of basic statements and of the methods in order to give to this field a better mathematical consistency, a deepening of the physical interpretations and significance, and the ability to provide powerful tools to extend the scientific study of many fields, especially in solid mechanics.

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