3

Principles of Thermodynamics

In this chapter, we discuss various fundamental concepts and results in continuum thermodynamics. Some examples are given in terms of the materials discussed in Part I, generalized to a nonisothermal context.

3.1 Heat Equation

Since the heat of a body is not conserved, we do not have a balance equation corresponding to those for mass and momentum, given by (1.3.1) and (1.3.12), respectively. However, there must be a balance between the net quantity of heat entering a body and the net heat absorbed by that body over a given time period.

We denote by $Q_A(t)$ the quantity of heat per unit time entering the subbody A of the body under consideration at time t by conduction or radiation. Also, let $H_A(t)$ be the heat absorbed by the subbody A per unit time at the moment t.

The heat flow density $c(\mathbf{x}, t) \in \mathbb{R}$ is assigned to each point $\mathbf{x}$ on the surface of the body. If $d\mathbf{a} = \mathbf{n}da$ is the area vector associated with a surface element on $\partial\varphi_t(A)$, the outward unit normal of which is $\mathbf{n}$, then $-cda$ is the amount of heat crossing da, going inward, per unit time. The quantity $c(\mathbf{x}, t)$ depends linearly on the orientation $\mathbf{n}$ of $d\mathbf{a}$; indeed, we have

$$c(\mathbf{x}, t) = \mathbf{q}(\mathbf{x}, t) \cdot \mathbf{n},$$

where $\mathbf{q} \in \mathbb{R}^3$ is known as the (Eulerian) heat flux vector. This is the analogue of Cauchy's theorem (1.3.24) for heat flow, where $\mathbf{q}$ corresponds to the Cauchy stress tensor. We can also define a heat flux vector $\mathbf{q}_L(\mathbf{X}, t)$ in the reference or Lagrangian configuration, corresponding to the first Piola–Kirchhoff stress tensor, given by (1.3.49). This quantity is given by

$$\mathbf{q}_L = J\mathbf{F}^{-1}\mathbf{q}. \tag{3.1.1}$$

It is an objective scalar, as defined by (1.4.7). The heat supply per unit time due to external sources, such as radiation, is denoted by $r(\mathbf{x}, t) \in \mathbb{R}$ or $\tilde{r}(\mathbf{X}, t)$ in the reference

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configuration. Then, for both configurations,

$$\begin{aligned}Q_A(t) &= -\int_{\partial\varphi_t(A)} \mathbf{q}(\mathbf{x},t)\cdot\mathbf{n}da + \int_{\varphi_t(A)} \rho(\mathbf{x},t)r(\mathbf{x},t)dv_t \\ &= -\int_{\partial\varphi_0(A)} \mathbf{q}_L(\mathbf{X},t)\cdot\mathbf{N}da_0 + \int_{\varphi_0(A)} \rho_0(\mathbf{X})\tilde{r}(\mathbf{X},t)dv_0,\end{aligned}$$

where $\mathbf{N}$ is the outward unit normal to $\partial\varphi_0(A)$. If we denote by $h(\mathbf{x},t)(\tilde{h}(\mathbf{X},t)$ in the Lagrangian description) the heat absorbed by the body per unit mass in unit time (specific heat power), then

$$H_A(t) = \int_{\varphi_t(A)} \rho(\mathbf{x},t)h(\mathbf{x},t)dv_t = \int_{\varphi_0(A)} \rho_0(\mathbf{X})\tilde{h}(\mathbf{X},t)dv_0.$$

At any time t and for any subbody A of the body, the heat equation is expressed by

$$H_A(t) = Q_A(t).$$

The Eulerian form of this equation is given by

$$\int_{\varphi_t(A)} \rho(\mathbf{x},t)h(\mathbf{x},t)dv_t = -\int_{\partial\varphi_t(A)} \mathbf{q}(\mathbf{x},t)\cdot\mathbf{n}da + \int_{\varphi_t(A)} \rho(\mathbf{x},t)r(\mathbf{x},t)dv_t, \tag{3.1.2}$$

from which, under hypotheses of continuity for the integrand functions and the arbitrariness of A, we can deduce the *Eulerian local form of the heat equation*

$$\rho(\mathbf{x},t)h(\mathbf{x},t) = -\operatorname{div}_{\mathbf{x}}\mathbf{q}(\mathbf{x},t) + \rho(\mathbf{x},t)r(\mathbf{x},t). \tag{3.1.3}$$

The Lagrangian form of (3.1.2) is

$$\int_{\varphi_0(A)} \rho_0(\mathbf{X})\tilde{h}(\mathbf{X},t)dv_0 = -\int_{\partial\varphi_0(A)} \mathbf{q}_L(\mathbf{X},t)\cdot\mathbf{n}da_0 + \int_{\varphi_0(A)} \rho_0(\mathbf{X})\tilde{r}(\mathbf{X},t)dv_0,$$

with corresponding local form

$$\rho_0(\mathbf{X})h(\mathbf{X},t) = -\mathrm{Div}_{\mathbf{X}}\mathbf{q}_L(\mathbf{X},t) + \rho_0(\mathbf{X})\tilde{r}(\mathbf{X},r).$$

3.2 Definition of a Material as a Dynamical System

For a large class of continuum systems, it is possible to obtain a good description of their thermomechanical properties using the concepts of *state* σ and *thermomechanic process* P. For such systems, it is necessary to introduce the concepts of *absolute temperature* θ and *gradient of temperature* $\mathbf{g} = \nabla_{\mathbf{x}}\theta$. The state is an entity that depends on material properties, while the process for any material is a function of time for a duration $d_P \in \mathbb{R}^+$ of type $P : [0, d_P) \to \mathrm{Lin}(\mathbb{R}^3)\times\mathbb{R}\times\mathbb{R}^3$, defined as

$$P(t) = \left(\mathbf{L}(t), \dot{\theta}(t), \mathbf{g}(t)\right). \tag{3.2.1}$$

Alternatively, there are advantages to using the Lagrangian description. In this case, $P : [0, d_P) \mapsto \mathrm{Sym} \times \mathbb{R} \times \mathbb{R}^3$ is given by

$$P(t) = \left(\dot{\mathbf{E}}(t), \dot{\theta}(t), \mathbf{g}_L(t)\right), \qquad \mathbf{g}_L = \nabla_{\mathbf{X}}\theta, \tag{3.2.2}$$

and is an objective scalar. In the present chapter, we use (3.2.1) for definiteness, though a choice closely related to (3.2.2) is adopted in Chap. 5.

Definition 3.2.1. *A material is simple if relative to a point* $\mathbf{X}$ *of the body* $\mathcal{B}$*, it is possible to define a state* σ *such that the constitutive equations for* $\mathbf{T}$*,* h*, and* $\mathbf{q}$ *are functions of* σ*,* P *and for which we have:*

(i) the space of states Σ *(that is, the set of possible states for the material body) is a metric space;*

(ii) any process $P : [0, d_P) \rightarrow \mathrm{Lin}(\mathbb{R}^3) \times \mathbb{R} \times \mathbb{R}^3$ *is a piecewise smooth function on* $[0, d_P)$ *and is in the space of processes* Π*; if* $P \in \Pi$*, then its restriction* $P_{[t_1,t_2)}$ *to the interval* $[t_1, t_2) \subset [0, d_P)$ *belongs to* Π*. The restriction* $P_{[0;t)}$ *is denoted by* P_t*.*
If $P_1, P_2 \in \Pi$*, then* $P_1 * P_2 \in \Pi$*, where*

$$P_1 * P_2(\tau) = \begin{cases} P_1(\tau), & \tau \in [0, d_{p_1}), \\ P_2(\tau - d_{p_1}), & \tau \in [d_{p_1}, d_{p_1} + d_{p_2}); \end{cases}$$

(iii) there exists a function $\hat{\varrho} : \Sigma \times \Pi \rightarrow \Sigma$*, the evolution function, which determines the final state* σ^f *when the initial state* σ^i *and the process* P *are known. Such a function has the semigroup property, that is, if* $(\sigma_1, \sigma_2) \in \Sigma$ *and* $P_1 \in \Pi$ *is such that* $\hat{\varrho}(\sigma_1, P_1) = \sigma_2$*, then for any* $P \in \Pi$*,*

$$\hat{\varrho}(\sigma_1, P_1 * P) = \hat{\varrho}(\hat{\varrho}(\sigma_1, P_1), P) = \hat{\varrho}(\sigma_2, P); \tag{3.2.3}$$

(iv) for any fixed $P \in \Pi$*, the function* $\hat{\varrho}(\cdot, P) : \Sigma \rightarrow \Sigma$ *is continuous.*

Remark 3.2.2. Referring in particular to (1.2.10), it is easy to prove that for thermoelastic materials, the function $\hat{\varrho}$ can be constructed as a general integral of the differential system

$$\frac{d\mathbf{F}}{dt} = \mathbf{LF}, \qquad \frac{d\theta}{dt} = \dot{\theta}, \tag{3.2.4}$$

and moreover, it is also easy to prove that (3.2.4) implies that $\hat{\varrho}(\cdot, P) : \Sigma \rightarrow \Sigma$ *is continuous. In a similar manner, the function* $\hat{\varrho}$ *can be determined for viscous fluids.*

The constitutive variables for a material depend on σ_t and $P(t)$, that is,

$$\begin{aligned} \mathbf{T}(t) &= \hat{\mathbf{T}}(\sigma_t, P(t)), \\ h(t) &= \hat{h}(\sigma_t, P(t)), \\ \mathbf{q}(t) &= \hat{\mathbf{q}}(\sigma_t, P(t)), \end{aligned} \tag{3.2.5}$$

where $\sigma_t = \hat{\varrho}(\sigma, P_t)$, the quantity P_t being the restriction of P to the time interval $[0, t) \subset [0, d_P)$ (see Definition 3.2.1).

For *thermoelastic materials*, we have the form

$$\mathbf{T}(t) = \hat{\mathbf{T}}(\mathbf{F}(t), \theta(t)), \quad h(t) = \mathbf{A}(\mathbf{F}, \theta) \cdot \mathbf{L} + B(\mathbf{F}, \theta)\dot{\theta}, \;\; \mathbf{q}(t) = -\mathbf{K}(\mathbf{F}, \theta)\mathbf{g}, \tag{3.2.6}$$

where $\hat{\mathbf{T}}$, $\mathbf{A}$, B, and $\mathbf{K}$ are continuous functions of $(\mathbf{F}, \theta)$. For these constitutive equations, the state is the pair $\sigma = (\mathbf{F}, \theta)$, and the space of possible states Σ will be a subspace of the vector space $\mathrm{Lin}(\mathbb{R}^3) \times \mathbb{R}$.

We also consider viscous fluids for which the thermomechanical characteristics are expressed by means of the constitutive equations (see (2.2.18))

$$\begin{aligned} \mathbf{T}(t) &= -p(\rho, \theta)\mathbf{I} + \lambda(\rho, \theta)(\mathrm{div}_{\mathbf{x}}\, \mathbf{v})\, \mathbf{I} + 2\mu(\rho, \theta)\mathbf{D}, \\ h(t) &= a(\rho, \theta)\dot{\rho} + b(\rho, \theta)\dot{\theta}, \qquad \mathbf{q}(t) = -K(\rho, \theta)\mathbf{g}, \end{aligned} \tag{3.2.7}$$

where p, λ, μ, a, b, and K are continuous functions of (ρ, θ). Here, the state is defined by the pair $\sigma = (\rho, \theta)$. Recalling (1.2.9), (1.2.23), and $(1.3.2)_2$, we see that the quantities $\dot{\rho}$, $\mathrm{div}_{\mathbf{x}}\, \mathbf{v} = \mathrm{tr}\nabla_{\mathbf{x}}\, \mathbf{v}$, and $\mathbf{D}$ are expressible in terms of $\mathbf{L}$, so that the Cauchy stress and the heat power will be functions of type $(3.2.5)_{1,2}$.

A limiting special case of viscous fluids, namely ideal fluids, will be considered in order to derive the *absolute temperature scale*. We deal only with the case that the fields are independent of the position variable $\mathbf{x}$. For such fluids, (3.2.7) reduces to

$$\mathbf{T}(t) = -p(\rho, \theta)\mathbf{I}, \qquad h(t) = a(\rho, \theta)\dot{\rho} + b(\rho, \theta)\dot{\theta}, \qquad \mathbf{q}(t) = \mathbf{0}. \tag{3.2.8}$$

The first and the second laws of thermodynamics introduced in the next two sections are constraints on the constitutive equations (3.2.5) rather than new equations imposed on the field variables. In other words, the constitutive equations (3.2.5) cannot depend in an arbitrary way on the variables $(\sigma_t, P(t))$. It is well known that it is impossible to devise a machine or a piece of equipment that executes a perpetual motion of the first or the second kind. Such a machine could be realized if it were possible to have materials with general constitutive equations of type (3.2.5). The principles of thermodynamics allow us to establish which materials, as described by equations of type (3.2.5), are compatible with the physical world.

3.3 First Principle of Thermodynamics

This principle leads to the law of conservation of energy under conditions whereby mechanical energy can be transformed into heat and vice versa.

Definition 3.3.1. *A closed cycle is a pair* $(\sigma, P) \in \Sigma \times \Pi$ *such that* $\hat{\varrho}(\sigma, P) = \sigma$.

- **First principle of thermodynamics for simple materials** (on cycles): *In any closed cycle* $(\sigma, P) \in \Sigma \times \Pi$, *the sum of the heat absorbed by the body and the work done by internal forces is equal to zero, that is,*

$$\int_0^{d_p} \left[\hat{h}(\sigma_t, P(t)) + \frac{1}{\rho}\hat{\mathbf{T}}(\sigma_t, P(t)) \cdot \mathbf{D}(t) \right] dt = 0. \tag{3.3.1}$$

Before dealing with the general case, let us consider a thermoelastic material represented by the system of equations (3.2.6). The space of states Σ is a particular subspace of the space $\mathrm{Lin}(\mathbb{R}^3) \times \mathbb{R}$. With any closed cycle (σ, P), we can associate the corresponding closed curve c in Σ given by

$$\sigma_t = \hat{\varrho}(\sigma, P_t), \qquad t \in [0, d_P).$$

The case in which c is a polygonal closed curve in Σ will be considered. Then, the integral in (3.3.1) takes the form

$$\int_0^{d_p} \left(\mathbf{A} \cdot \mathbf{L} + B\dot{\theta} + \frac{1}{\rho} \mathbf{T} \cdot \mathbf{D} \right) dt = 0,$$

which can be rewritten as a curvilinear integral in the space of states Σ in the form

$$\int_c \mathbf{A} \left(\mathbf{F}^{-1} \right)^T \cdot d\mathbf{F} + B d\theta + \frac{1}{\rho} \mathbf{T} \left(\mathbf{F}^{-1} \right)^T \cdot d\mathbf{F} = 0, \tag{3.3.2}$$

where (3.2.4) has been used. This is the integral on c of the following differential form:

$$\left(\mathbf{A} + \frac{1}{\rho} \mathbf{T} \right) \left(\mathbf{F}^{-1} \right)^T \cdot d\mathbf{F} + B d\theta. \tag{3.3.3}$$

On the basis of (3.3.2), one can assert that the differential form (3.3.3) is integrable. This means that under hypotheses of continuity for $\mathbf{A}$, $\mathbf{T}$, and B, there exists a function of state $e : \Sigma \to \mathbb{R}$, differentiable on Σ and such that

$$de = \left(\mathbf{A} + \frac{1}{\rho} \mathbf{T} \right) \left(\mathbf{F}^{-1} \right)^T \cdot d\mathbf{F} + B d\theta. \tag{3.3.4}$$

It is possible to obtain an analogous result by repeating the above procedure for an ideal or viscous fluid. These observations lead to the idea that it is always possible to prove the existence of a function of such a type for any simple material.

The disadvantage of (3.3.1) is that for materials with memory, which are our main concern in later chapters, closed cycles rarely occur. We now state, without proof, the first law for a general material, in a form that makes no reference to cycles.

- **The first principle of thermodynamics** (general form): *For any simple material, there exists a function of state $e : \Sigma \to \mathbb{R}$, known as the internal energy, such that for any pair of states $\sigma_1, \sigma_2 \in \Sigma$ and for any process P with $\hat{\varrho}(\sigma_1, P) = \sigma_2$, one has*

$$e(\sigma_2) - e(\sigma_1) = \int_0^{d_P} \left[\hat{h}(\sigma_t, P(t)) + \frac{1}{\rho} \hat{\mathbf{T}}(\sigma_t, P(t)) \cdot \mathbf{L}(t) \right] dt, \tag{3.3.5}$$

where $\sigma_t = \hat{\varrho}(\sigma_1, P_t)$.

Remark 3.3.2. The internal energy e is uniquely determined up to an additive constant, which can be fixed by assigning the value of the energy in the reference state of the material. We refer to e as *a thermodynamic potential*.

At all points of continuity of the function

$$\hat{h}(\sigma_t, P(t)) + \frac{1}{\rho}\hat{\mathbf{T}}(\sigma_t, P(t)) \cdot \mathbf{L}(t),$$

it follows from (3.3.5) that

$$\frac{de}{dt}(\sigma_t) = \hat{h}(\sigma_t, P(t)) + \frac{1}{\rho}\hat{\mathbf{T}}(\sigma_t, P(t)) \cdot \mathbf{L}(t). \tag{3.3.6}$$

Moreover, using the heat equation (3.1.3), we obtain the *energy equation*

$$\rho\frac{de}{dt}(\sigma_t) = -\mathrm{div}_{\mathbf{x}}\, \hat{\mathbf{q}}(\sigma_t, P(t)) + \hat{\mathbf{T}}(\sigma_t, P(t)) \cdot \mathbf{L}(t) + \rho r. \tag{3.3.7}$$

Remark 3.3.3. Note that (3.3.6) allows us to express the quantity h in terms of the new function of state e and the mechanical rate of work. Indeed, we can now regard e as a fundamental quantity, more convenient than $\hat{h}$ because it is a function of state.

In Chap. 5, we will use the Lagrangian form of (3.3.7), given by

$$\rho_0\dot{e}(\sigma_t) = -\mathrm{Div}_{\mathbf{X}}\hat{\mathbf{q}}_L\,(\sigma_t, P(t)) + \widehat{\mathbf{S}}(\sigma_t, P(t)) \cdot \dot{\mathbf{E}}(t) + \rho_0 r, \tag{3.3.8}$$

where $\widehat{\mathbf{S}}$ is the second Piola–Kirchhoff stress tensor, defined by (1.3.52), and $\mathbf{E}$ is the strain tensor given by $(1.2.21)_1$.

3.4 Second Principle of Thermodynamics

The first principle of thermodynamics allows the possibility of transformation of various types of energy from one into another, provided the total energy is conserved. The second principle of thermodynamics imposes some limits on such transformations of energy and asserts that not all types of energy have the same capability of transforming themselves into mechanical work. These two assertions are not in contradiction. In fact, for the first principle we can prove the existence of an energetic balance, while the second principle asserts that natural transformations, for a system in a cycle, are those that transform valuable energy into a less valuable form. In other words, this means that in such processes there is a loss of energy.

3.4.1 The Absolute Temperature Scale

Before discussing general materials, we briefly consider perfect fluids with field variables that are independent of the position variable $\mathbf{x}$, defined by the constitutive equations (3.2.8), in order to derive the absolute temperature scale and to motivate the general definition of entropy.

With the aid of (3.2.8), the heat equation (3.1.3) can be written as

$$\rho\left[a(\rho, \theta)\dot{\rho} + b(\rho, \theta)\dot{\theta}\right] = \rho r, \tag{3.4.1}$$

where θ in this relationship is some empirical temperature. For materials with dissipation, the entropy relationship will be an inequality, as we shall see below. However, for a perfect fluid, it will be an equality, which is assumed to be of the form

$$\rho\dot{\eta} = -div_{\mathbf{x}}\mathbf{j}_{\eta} + \rho s, \tag{3.4.2}$$

where $\mathbf{j}_{\eta}$ is a flux term describing entropy flow and s is an entropy source term. We can neglect the divergence term due to the assumption of field homogeneity, so that (3.4.2) becomes

$$\begin{gathered}\rho\left[c(\rho,\theta)\dot{\rho} + d(\rho,\theta)\dot{\theta}\right] = \rho s,\\ c(\rho,\theta) = \frac{\partial\eta(\rho,\theta)}{\partial\rho}, \qquad d(\rho,\theta) = \frac{\partial\eta(\rho,\theta)}{\partial\theta}.\end{gathered} \tag{3.4.3}$$

We do not regard this equation as independent of the heat equation (3.4.1) but rather as a nontrivial relation that can be derived from that equation, so that any solution of the entropy equation is also a solution of the heat equation. Thus, we suppose the existence of an integrating factor $R(\rho,\theta)$ such that

$$c(\rho,\theta)\dot{\rho} + d(\rho,\theta)\dot{\theta} - s = R(\rho,\theta)\left[a(\rho,\theta)\dot{\rho} + b(\rho,\theta)\dot{\theta} - r\right]$$

for any $\dot{\rho}$, $\dot{\theta}$, and r. It follows that

$$c = Ra, \qquad d = Rb, \qquad s = Rr. \tag{3.4.4}$$

We now show that the factor R does not depend on ρ and is a monotonic decreasing function of θ. In relation $(3.4.4)_3$, the quantities s and r are source terms and do not depend on the material properties.

Let us now consider a further special case that of an ideal fluid. This is a fluid with internal energy depending only on temperature and a pressure function $p(\rho,\theta)$ that is a monotonic increasing function of θ.

Now (3.3.6), with the aid of $(1.3.2)_2$, yields

$$h(\rho,\theta,P(t)) = e'(\theta)\dot{\theta} - \frac{1}{\rho^2}p(\rho,\theta)\dot{\rho},$$

which, combined with $(3.2.8)_2$, gives

$$a(\rho,\theta) = -\frac{1}{\rho^2}p(\rho,\theta), \qquad b(\rho,\theta) = b(\theta) = e'(\theta),$$

whence $(3.4.4)_{1,2}$ become

$$c(\rho,\theta) = -\frac{R(\theta)}{\rho^2}p(\rho,\theta), \qquad d(\rho,\theta) = d(\theta) = R(\theta)b(\theta). \tag{3.4.5}$$

From $(3.4.5)_2$ and $(3.4.3)_{2,3}$, we conclude that

$$\eta(\rho,\theta) = A(\rho) + B(\theta),$$

where

$$A'(\rho) = -\frac{R(\theta)}{\rho^2} p(\rho, \theta), \qquad B'(\theta) = d(\theta) = R(\theta)b(\theta).$$

Thus, $R(\theta)p(\rho, \theta)$ cannot depend on θ. Let θ' be a fixed temperature. Then,

$$R(\theta) = R(\theta')\frac{p(\rho, \theta')}{p(\rho, \theta)}.$$

We can always choose $R(\theta') > 0$. The quantities $p(\rho, \theta')$ and $p(\rho, \theta)$ both are positive, and the latter increases monotonically with θ. Thus, R is a positive decreasing function of the empirical temperature θ.

Recalling $(3.4.4)_3$ and the fact that the source functions s and r do not depend on the material under consideration, we deduce from $(3.4.4)_3$ that R has a universal character. Its inverse

$$T(\theta) = \frac{1}{R(\theta)}$$

is positive and increasing and can be chosen as a suitable measure of temperature. This function represents *the absolute temperature scale*.

Dropping the constancy assumption with respect to $\mathbf{x}$ on the fields, $(3.4.4)_3$, (3.1.3), and (3.4.2) give

$$R(\theta)(\rho h + \operatorname{div}_{\mathbf{x}} \mathbf{q}) = \rho\dot{\eta} + \operatorname{div}_{\mathbf{x}} \mathbf{j}_\eta,$$

which must hold for all choices of fields. Using the identity

$$R(\theta)\operatorname{div}_{\mathbf{x}} \mathbf{q} = \operatorname{div}_{\mathbf{x}} [R(\theta)\mathbf{q}] - \mathbf{q} \cdot \nabla R(\theta),$$

we deduce that

$$\operatorname{div}_{\mathbf{x}} \mathbf{j}_\eta = \operatorname{div}_{\mathbf{x}}(R\mathbf{q}), \qquad \rho\dot{\eta} = \rho R h - \mathbf{q} \cdot \nabla R(\theta). \tag{3.4.6}$$

From now on, we denote the absolute temperature $1/R$ by θ. The relations in (3.4.6) provide motivation for those now introduced, though the former were derived for very particular materials.

3.4.2 Entropy Action

We consider the function

$$s(\sigma, P) = \int_0^{d_P} \left[\frac{\hat{h}(\sigma_t, P(t))}{\theta(t)} + \frac{1}{\rho\theta^2(t)}\hat{\mathbf{q}}(\sigma_t, P(t)) \cdot \mathbf{g}(t)\right] dt, \tag{3.4.7}$$

which will be referred to as the *entropy action*. By means of this functional we can introduce the following principle:

- **The second principle of thermodynamics for simple materials** (on cycles): *On any closed cycle* $(\sigma, P) \in \Sigma \times \Pi$, *the entropy action is such that*

$$\oint_0^{d_P} \left[\frac{\hat{h}(\sigma_t, P(t))}{\theta(t)} + \frac{1}{\rho\theta^2(t)}\hat{\mathbf{q}}(\sigma_t, P(t)) \cdot \mathbf{g}(t)\right] dt \le 0. \tag{3.4.8}$$

Remark 3.4.1. For a homogeneous process ($\mathbf{g} = \mathbf{0}$), relation (3.4.8) takes the classical form

$$\oint_0^{d_P} \frac{\hat{h}(\sigma_t, P(t))}{\theta(t)} dt \leq 0.$$

Consider (3.4.8) for isothermal processes. If we set $\theta = constant$ and use (3.3.1), then it follows that

$$-\frac{1}{\theta} \oint_0^{d_P} \frac{1}{\rho} \hat{\mathbf{T}}(\sigma_t, P(t)) \cdot \mathbf{D}(t) dt \leq 0, \tag{3.4.9}$$

which is a statement that the mechanical work is nonnegative in closed processes or the principle of dissipation of mechanical energy (see (1.3.33) or (2.3.14)in the material description).

For a general material, the second law is now stated, again without proof and making no reference to closed processes.

- **The second principle of thermodynamics (general form)**: *There exists a function of state* $\eta : \Sigma \to \mathbb{R}$, *known as the entropy, such that*

$$\eta(\sigma_2) - \eta(\sigma_1) \geq \oint_0^{d_P} \left(\frac{h}{\theta} + \frac{1}{\rho\theta^2} \mathbf{q} \cdot \mathbf{g} \right) dt = s(\sigma_1, P), \tag{3.4.10}$$

for all $(\sigma_1, \sigma_2) \in \Sigma$ *and* $P \in \Pi$ *with* $\hat{\varrho}(\sigma_1, P) = \sigma_2$.

Remark 3.4.2. Under appropriate hypotheses of regularity on the constitutive functionals, it follows from the inequality (3.4.10) that

$$\dot{\eta}(\sigma_t) \geq \frac{\hat{h}(\sigma_t, P(t))}{\theta(t)} + \frac{1}{\rho(t)\theta^2(t)} \hat{\mathbf{q}}(\sigma_t, P(t)) \cdot \mathbf{g}(t). \tag{3.4.11}$$

We note the connection between this inequality and the equality $(3.4.6)_2$. By means of the heat equation (3.1.3), we deduce from relation (3.4.11) the well-known Clausius–Duhem inequality

$$\rho\dot{\eta} \geq -\mathrm{div}_{\mathbf{x}} \left(\frac{\mathbf{q}}{\theta} \right) + \frac{\rho}{\theta} r. \tag{3.4.12}$$

Again, we observe the connection between this relation and (3.4.2) combined with $(3.4.6)_1$.

Let us define the function of state known as the *Helmholtz free energy* by

$$\psi_H(\sigma_t) = e(\sigma_t) - \theta(t)\eta(\sigma_t). \tag{3.4.13}$$

Using (3.3.7), (3.4.12), and (3.4.13), one can show that

$$\dot{\psi}_H(\sigma_t) \leq \frac{1}{\rho(t)} \hat{\mathbf{T}}(\sigma_t, P(t)) \cdot \mathbf{L}(t) - \eta(\sigma_t)\dot{\theta}(t) - \frac{1}{\rho(t)\theta(t)} \hat{\mathbf{q}}(\sigma_t, P(t)) \cdot \mathbf{g}(t), \tag{3.4.14}$$

which is an alternative form of the Clausius–Duhem inequality. The free energy function of state is not uniquely determined in general, for a given material. Very general properties of this function are proved in the next chapter, including the result that the free energies associated with a given state of the material with memory form a convex set. This nonuniqueness also applies to entropy.

In Chap. 5, we will use the Lagrangian form of (3.4.12) and (3.4.14), given by

$$\rho_0\dot{\eta} \geq -\mathrm{Div}_{\mathbf{X}}\left(\frac{\mathbf{q}_L}{\theta}\right) + \frac{\rho_0}{\theta}r \tag{3.4.15}$$

and

$$\dot{\psi}_H(\sigma_t) \leq \frac{1}{\rho_0}\widehat{\mathbf{S}}(\sigma_t, P(t)) \cdot \dot{\mathbf{E}}(t) - \eta(\sigma_t)\dot{\theta}(t) - \frac{1}{\rho_0\theta(t)}\hat{\mathbf{q}}_L(\sigma_t, P(t)) \cdot \mathbf{g}_L(t), \tag{3.4.16}$$

where $\mathbf{g}_L$ is given by (3.1.1).

We now consider two examples: nonlinear elastic bodies and viscous liquids, already introduced in an isothermal context in Part I. Recalling Remark 3.3.3, it will be observed that we use the heat power h but immediately relate it to the internal energy. In the second example, h is not introduced; instead, e is used.

The principles of thermodynamics impose some restrictions on the constitutive functionals. They become automatically satisfied if the constitutive equations obey certain conditions. In what follows, we seek to determine such conditions for the constitutive equations describing elastic materials and viscous fluids.

3.5 Applications to Elastic Bodies

For an elastic body, we have $\sigma = (\mathbf{F}, \theta)$, while from (3.2.6) and (3.3.5), for any $(\sigma, P) \in \Sigma \times \Pi$, where $\hat{\varrho}(\sigma, P) = \sigma_1$,

$$e(\sigma_1) - e(\sigma) = \int_0^{d_P} \left[B(\mathbf{F}, \theta)\dot{\theta} + \mathbf{A}(\mathbf{F}, \theta) \cdot \mathbf{L} + \frac{1}{\rho(\mathbf{F})}\mathbf{T}(\mathbf{F}, \theta) \cdot \mathbf{L} \right] dt.$$

From (3.3.6) (indeed, more specifically recalling (3.3.4)), we have that $e = \tilde{e}(\mathbf{F}, \theta)$ obeys the relation

$$\frac{d\tilde{e}}{dt}(\mathbf{F}, \theta) = B(\mathbf{F}, \theta)\dot{\theta} + \mathbf{A}(\mathbf{F}, \theta) \cdot \mathbf{L} + \frac{1}{\rho(\mathbf{F})}\mathbf{T}(\mathbf{F}, \theta) \cdot \mathbf{L}.$$

The function (3.4.7) can be written as

$$s(\sigma, P) = \int_0^{d_P} \left\{ \frac{1}{\theta}\left[-\frac{1}{\rho}\hat{\mathbf{T}}(\mathbf{F}, \theta) \cdot \mathbf{L} + \frac{\partial \tilde{e}}{\partial \mathbf{F}} \cdot \dot{\mathbf{F}} + \frac{\partial \tilde{e}}{\partial \theta}\dot{\theta} \right] + \frac{1}{\rho\theta^2}\hat{\mathbf{q}}(\mathbf{F}, \theta; \mathbf{g}) \cdot \mathbf{g} \right\} dt.$$

We now consider the integral on an arbitrary curve c in $\mathrm{Lin}(\mathbb{R}^3) \times \mathbb{R}$,

$$I(c) = \int_c \frac{1}{\theta}\left[B(\mathbf{F}, \theta)d\theta + \mathbf{A}(\mathbf{F}, \theta)\left(\mathbf{F}^T\right)^{-1} \cdot d\mathbf{F} \right]. \tag{3.5.1}$$

If c^+ is a closed curve in $\mathrm{Lin}(\mathbb{R}^3) \times \mathbb{R}$ and c^- is the same curve with opposite orientation, then

$$I(c^+) = -I(c^-). \tag{3.5.2}$$

Let $\sigma \in \Sigma$ be a finite element, and let c^+ be an oriented closed polygonal curve containing σ. Then for any $t > 0$, there is a parametrization $\tau \to (\mathbf{F}(\tau), \theta(\tau))$ of the curve c^+, defined on $[0, d_P)$, such that

$$(\mathbf{F}(d_P), \theta(d_P)) = (\mathbf{F}(0), \theta(0)) = \sigma.$$

Corresponding to this parametrization, there is a process P such that

$$\hat{\varrho}(\sigma, P_t) = (\mathbf{F}(t), \theta(t)), \quad \hat{\varrho}(\sigma, P) = \sigma.$$

Using this parametrization of c^+, we can rewrite (3.5.1) in the form

$$I(c^+) = \int_0^{d_p} \frac{1}{\theta(t)} \left[B(\mathbf{F}, \theta)\dot{\theta} + \mathbf{A}(\mathbf{F}, \theta) \left(\mathbf{F}^T\right)^{-1} \cdot \dot{\mathbf{F}} \right] dt = \int_0^{d_P} \frac{\hat{h}\left(\mathbf{F}, \theta, \dot{\mathbf{F}}, \dot{\theta}\right)}{\theta} dt,$$

by virtue of $(3.2.6)_2$. The second principle of thermodynamics (3.4.8) states that on any closed process P with duration d_P, we have

$$\int_0^{d_P} \frac{\hat{h}}{\theta} dt + \int_0^{d_P} \frac{1}{\rho\theta^2} \hat{\mathbf{q}} \cdot \mathbf{g} dt \leq 0. \tag{3.5.3}$$

Therefore, we obtain

$$I(c^+) \leq -\int_0^{d_P} \frac{1}{\rho\theta^2} \hat{\mathbf{q}} \cdot \mathbf{g} dt. \tag{3.5.4}$$

If we set $M(c^+) = \sup\{-\frac{1}{\rho\theta^2} \hat{\mathbf{q}}(\mathbf{F}, \theta, \mathbf{g}) \cdot \mathbf{g} \mid (\mathbf{F}, \theta) \in c^+\}$, then $M(c^+)$ is finite because c^+ is a compact subset of Σ and $\mathbf{q}$ is assumed continuous on Σ. Moreover, $\hat{\mathbf{q}}(\mathbf{F}, \theta, \mathbf{g}) \cdot \mathbf{g}$ is always nonpositive for an elastic body. In fact, if we consider the process P defined by

$$P(t) \equiv (\mathbf{0}, 0, \mathbf{g}) \quad \text{for all } t \in [0, d_P)$$

and suppose that the initial state is $\sigma_0 = (\mathbf{F}, \theta)$, where $\mathbf{g}$, $\mathbf{F}$, and θ are arbitrary given quantities, independent of t, then from (3.5.3), we have

$$\hat{\mathbf{q}}(\mathbf{F}, \theta, \mathbf{g}) \cdot \mathbf{g} \leq 0 \quad \text{for all } (\mathbf{F}, \theta, \mathbf{g}). \tag{3.5.5}$$

Therefore, from (3.5.4),

$$I(c^+) \leq d_P M(c^+),$$

and since this relation holds for any $d_P > 0$, we obtain that

$$I(c^+) \leq 0.$$

Let us now consider the curve c^- with opposite orientation with respect to c^+. Using a procedure similar with that leading to (3.5.5), we obtain

$$I(c^-) \leq 0,$$

and hence, by virtue of (3.5.2), on any closed curve c,

$$I(c) = 0.$$

Therefore, using well-known theorems concerning the integrability of differential forms, we deduce from (3.5.1) that there exists a differentiable function of state $\eta : \Sigma \to R$, such that

$$\dot{\eta}(\mathbf{F}, \theta) = \frac{1}{\theta(t)} \left[B(\mathbf{F}, \theta)\dot{\theta} + \mathbf{A}(\mathbf{F}, \theta) \left(\mathbf{F}^T\right)^{-1} \cdot \dot{\mathbf{F}} \right] = \frac{\hat{h}(\mathbf{F}, \theta, \dot{\mathbf{F}}, \dot{\theta})}{\theta}. \tag{3.5.6}$$

Using $(3.5.6)_2$, we can write the expression (3.4.7) for $s(\sigma, P)$ as

$$s(\sigma, P) = \eta(\hat{\rho}(\sigma, P)) - \eta(\sigma) + \int_0^{d_P} \frac{1}{\rho\theta^2} \hat{\mathbf{q}}(\sigma_t, P(t)) \cdot \mathbf{g} dt,$$

so that using the fact that $\mathbf{q} \cdot \mathbf{g} \leq 0$, we obtain

$$s(\sigma, P) \leq \eta(\hat{\rho}(\sigma, P)) - \eta(\sigma).$$

Also, from $(3.5.6)_2$, the property $\mathbf{q} \cdot \mathbf{g} \leq 0$, and (3.1.3), we recover the Clausius–Duhem inequality (3.4.12):

$$\rho\dot{\eta} \geq \frac{1}{\theta}\rho h + \frac{1}{\theta^2}\mathbf{q} \cdot \mathbf{g} = \frac{1}{\theta}\left(-\mathrm{div}_{\mathbf{x}}\, \mathbf{q} + \rho r + \frac{1}{\theta}\mathbf{q} \cdot \mathbf{g}\right) = -\mathrm{div}_{\mathbf{x}} \left(\frac{\mathbf{q}}{\theta}\right) + \frac{\rho}{\theta} r.$$

3.6 Thermodynamic Restrictions for Viscous Fluids

We consider here the compressible flow of a Newtonian fluid defined by the constitutive equations (3.2.7) and determine the restrictions imposed by the principles of thermodynamics on these equations. Combining (3.3.6) and (3.4.11), we obtain

$$\theta\dot{\eta} \geq \dot{e} - \frac{1}{\rho}\mathbf{T} \cdot \mathbf{L} + \frac{1}{\rho\theta}\mathbf{q} \cdot \mathbf{g}.$$

Recalling that for viscous fluids the state is given by the pair $\sigma = (\rho, \theta)$, it follows that the internal energy e and entropy η are functions of the following type:

$$e = \hat{e}(\rho, \theta), \quad \eta = \hat{\eta}(\rho, \theta).$$

As noted earlier for e, these quantities are referred to as thermodynamic potentials.

The function of state introduced in (3.4.13), namely the Helmholtz free energy ψ_H, is also a thermodynamic potential, which here assumes the form

$$\hat{\psi}_H(\rho, \theta) = \hat{e}(\rho, \theta) - \theta\hat{\eta}(\rho, \theta).$$

It must satisfy (3.4.14):

$$\dot{\psi}_H \leq -\eta\dot{\theta} + \frac{1}{\rho}\mathbf{T}\cdot\mathbf{L} - \frac{1}{\rho\theta}\mathbf{q}\cdot\mathbf{g}. \tag{3.6.1}$$

On the basis of the principles of thermodynamics, the inequality (3.6.1) must be verified by all processes $P(t) = \left(\mathbf{L}(t), \dot{\theta}(t), \mathbf{g}(t)\right)$ representing possible solutions of the equation of motion. Recalling (1.2.23), the symmetry of $\mathbf{T}$, and in particular its form given by $(3.2.7)_1$, we can write (3.6.1) in the form

$$\frac{\partial\psi_H}{\partial\rho}\dot{\rho} + \frac{\partial\psi_H}{\partial\theta}\dot{\theta} \leq -\eta\dot{\theta} + \frac{1}{\rho}\Big[-p\,\mathrm{div}_{\mathbf{x}}\,\mathbf{v} + \lambda\,(\mathrm{div}_{\mathbf{x}}\,\mathbf{v})^2 + 2\mu|\mathbf{D}|^2\Big] + \frac{1}{\rho\theta}K|\mathbf{g}|^2. \tag{3.6.2}$$

With the aid of the equation of continuity $(1.3.2)_2$, relation (3.6.2) gives

$$\left(\frac{\partial\psi_H}{\partial\rho} - \frac{p}{\rho^2}\right)\dot{\rho} + \left(\frac{\partial\psi_H}{\partial\theta} + \eta\right)\dot{\theta} \leq \frac{\lambda}{\rho^3}\dot{\rho}^2 + \frac{2\mu}{\rho}|\mathbf{D}|^2 + \frac{K}{\rho\theta}|\mathbf{g}|^2. \tag{3.6.3}$$

The quantities ψ_H, p, η, λ, μ, and K are functions of the state (ρ,θ). For a given state (ρ,θ), we consider a process P,

$$P(t) = (\mathbf{0}, \dot{\theta}, \mathbf{0}),$$

for some arbitrary $\dot{\theta}$. In this case, since $\mathbf{L} = \mathbf{0}$ yields $\mathbf{D} = \mathbf{0}$, it follows that $\mathrm{div}_{\mathbf{x}}\,\mathbf{v} = \mathrm{tr}\nabla_{\mathbf{x}}\,\mathbf{v} = 0$, and hence $\dot{\rho} = 0$ by virtue of (1.2.9), (1.2.23), and $(1.3.2)_2$, relation (3.6.3) reduces to

$$\left(\frac{\partial\psi_H}{\partial\theta} + \eta\right)\dot{\theta} \leq 0,$$

from which, in view of the fact that $\dot{\theta}$ is arbitrary, we deduce that

$$\eta(\rho,\theta) = -\frac{\partial\psi_H}{\partial\theta}(\rho,\theta). \tag{3.6.4}$$

Now consider a process of the type

$$P(t) = \left(\left(\frac{1}{3}div_{\mathbf{x}}\,\mathbf{v}\right)\mathbf{I}, 0, \mathbf{0}\right) = \left(-\frac{\dot{\rho}}{3\rho}\mathbf{I}, 0, \mathbf{0}\right). \tag{3.6.5}$$

Then (3.6.3) yields

$$\left(\frac{\partial\psi_H}{\partial\rho} - \frac{p}{\rho^2}\right)\dot{\rho} \leq \frac{1}{\rho^3}\left(\lambda + \frac{2}{3}\mu\right)\dot{\rho}^2,$$

where $\dot{\rho}$ is arbitrary. Dividing by the quantity $\dot{p}^2$ and using the fact that $\dot{\rho}$ is arbitrary, we see that this inequality holds if and only if

$$p = \rho^2\frac{\partial\psi_H}{\partial\rho}. \tag{3.6.6}$$

With these results, the initial inequality (3.6.3) reduces to

$$\frac{\lambda}{\rho^3}\dot{\rho}^2 + \frac{2\mu}{\rho}|\mathbf{D}|^2 + \frac{K}{\rho\theta}|\mathbf{g}|^2 \geq 0. \tag{3.6.7}$$

Taking into account the arbitrariness of $\dot{\rho}$, $\mathbf{D}$, and $\mathbf{g}$, we obtain, from (3.6.7), the following inequalities:

$$\frac{K}{\rho\theta}|\mathbf{g}|^2 \geq 0, \qquad \frac{\lambda}{\rho^3}\dot{\rho}^2 + \frac{2\mu}{\rho}|\mathbf{D}|^2 \geq 0. \tag{3.6.8}$$

The first inequality in (3.6.8) furnishes the condition

$$K \geq 0. \tag{3.6.9}$$

If we first set $\mathbf{D} = \frac{1}{3}\,(\mathrm{div}_{\mathbf{x}}\,\mathbf{v})\,\mathbf{I}$ (see (3.6.5)) in the second inequality of (3.6.8), then

$$\left(\lambda + \frac{2}{3}\mu\right)(\mathrm{div}_{\mathbf{x}}\,\mathbf{v})^2 \geq 0,$$

from which we deduce that

$$3\lambda + 2\mu \geq 0. \tag{3.6.10}$$

If we now choose $\mathbf{D}$ arbitrarily but put $\mathrm{div}_{\mathbf{x}}\,\mathbf{v} = 0$ so that $\dot{\rho} = 0$, then the second inequality of (3.6.8) yields

$$\mu \geq 0. \tag{3.6.11}$$

Therefore, the restrictions imposed by the principles of thermodynamics on the constitutive equation for compressible flow of a Newtonian fluid defined by the constitutive equation (3.2.7) are those contained in relations (3.6.4), (3.6.6), (3.6.9), (3.6.10), and (3.6.11).

We have used as examples in this chapter the classical materials introduced in Part I. However, the main focus of later chapters will be on more general materials, namely those with memory. The principles of thermodynamics introduced here and their consequences in the form of the energy equation (3.3.7) or (3.3.8) and the Clausius–Duhem inequality (3.4.14) or (3.4.16) apply quite generally to simple materials, and indeed we will use them in Chap. 5. In fact, general constitutive equations for materials with memory are derived using a generalization of the kind of arguments developed in Sect. 3.6 to obtain (3.6.4) and (3.6.6).

The statements of the thermodynamic principles that we have presented in these sections apply to simple materials. In the next section we study the generalization of the laws of thermodynamics required for nonsimple materials.

3.7 Principles of Thermodynamics for Nonsimple Materials

Just as for a simple material, we suppose that a nonsimple material is formally characterized by a state σ, which is an element of the space Σ of the possible states of the body, and a process P, belonging to the space Π of the possible processes of the body, with a duration $d_P \in \mathbb{R}^+$, defined more generally than by (3.2.1). Furthermore, we assume that for this system, there exists a function $\hat{\rho} \in \Sigma \times \Pi \to \Sigma$ with the same properties as described in Definition 3.2.1. Finally, the behavior of the material is always described by the triplet $(\mathbf{T}, h, \mathbf{q})$, defined in (3.2.6).

The important difference between simple and nonsimple materials, from a thermodynamic point of view, emerges in the context of defining the mechanical power.

For simple materials, the internal mechanical power, denoted by $\mathcal{P}^i_m$, is always expressed by

$$\mathcal{P}^i_m = \mathbf{T} \cdot \mathbf{L}, \tag{3.7.1}$$

and therefore the first law assumes the form (3.3.1) or (3.3.7).

In the general case, this quantity is not necessarily defined by (3.7.1). Its expression can be derived by means of the balance equation of power.

For a mechanical system, denoting by $\tilde{\mathcal{P}}^i_m$ the internal mechanical power, this balance equation is written as

$$\frac{d}{dt}T(t) + \tilde{\mathcal{P}}^i_m(\sigma(t), P(t)) = \tilde{\mathcal{P}}^e_m, \tag{3.7.2}$$

where $\tilde{\mathcal{P}}^e_m$ denotes the external mechanical power, defined by the flux and the mechanical sources due to external forces, while T is the kinetic energy.

3.7.1 First Law of Thermodynamics

For nonsimple mechanical systems, the first law is stated by assuming the existence of a function of state $e(\sigma)$, the internal energy, such that

$$\rho\dot{e}(\sigma(t)) = \tilde{\mathcal{P}}^i_m(\sigma(t), P(t)) + \rho h(\sigma(t), P(t)), \tag{3.7.3}$$

where h denotes the internal thermal power per unit mass and ρ is the mass density.

The form (3.7.3) is the classical statement of the first law, given by R. Clausius in 1850, and can be applied also to electromagnetic, chemical, and biological systems, which are characterized by the triplet $(\Sigma, \Pi, \hat{\rho})$.

An alternative and more general formulation of the first law is now given.

• **First principle of thermodynamics** (on cycles). *For any cyclic process* (σ^i, P), *i.e.*, $\hat{\rho}(\sigma^i, P) = \sigma^i$, *the sum of the internal thermal power* ρh *and of other internal powers* $\tilde{\mathcal{P}}^i(\sigma, P)$ *satisfies*

$$\oint \left[\tilde{\mathcal{P}}^i(\sigma(t), P(t)) + \rho h(\sigma(t), P(t))\right] dt = 0, \tag{3.7.4}$$

where $\sigma(t) = \hat{\rho}(\sigma^i, P_t)$.

Referring to (3.3.4), we note that it is similarly possible to deduce from (3.7.4) the existence of an internal energy $e(\sigma(t))$ such that the equality (3.7.3) holds.

An example is now formulated for which, in the representation of the first law, we cannot use the expression (3.7.1) for the internal mechanical power.

Let us consider a thermoelastic plate, for which, following [116, 225, 226] (see also [3]), the stress tensor (in this context a vector) assumes the form

$$\mathbf{T}(\mathbf{x}, t) = -a\nabla\left[\nabla^2 u(\mathbf{x}, t)\right] + b\nabla\ddot{u}(\mathbf{x}, t) + c\nabla\theta(\mathbf{x}, t), \tag{3.7.5}$$

where u is the vertical displacement, while a, b, and c are suitable material constants. The equation of motion is given by

$$\rho\ddot{u}(\mathbf{x},t) = \nabla\cdot\mathbf{T}(\mathbf{x},t) + \rho f(\mathbf{x},t), \tag{3.7.6}$$

where f denotes the external forces. We multiply this by $\dot{u}$ to obtain

$$\frac{d}{dt}\left(\frac{1}{2}\rho\dot{u}^2\right) = \nabla\cdot(\mathbf{T}\dot{u}) - \mathbf{T}\cdot\nabla\dot{u} + \rho f\dot{u}. \tag{3.7.7}$$

To derive the contribution due to the internal and external powers in the balance equation (3.7.7), we must use the representation (3.7.5) for the stress $\mathbf{T}$. Then (3.7.7) becomes

$$\begin{aligned}&\frac{1}{2}\frac{d}{dt}\left[\rho\dot{u}^2 + a\left(\nabla^2 u\right)^2 + b\left(\nabla\dot{u}\right)^2\right] + c\nabla\theta\cdot\nabla\dot{u}\\ &\quad = \nabla\cdot\left\{\left[-a\nabla\left(\nabla^2 u\right) + b\nabla\ddot{u} + c\nabla\theta\right]\dot{u} + a\nabla^2 u\nabla\dot{u}\right\} + \rho f\dot{u}.\end{aligned} \tag{3.7.8}$$

On comparing with (3.7.2), it follows that the internal mechanical power is given by

$$\tilde{\mathcal{P}}^i_m = \frac{1}{2}\frac{d}{dt}\left[a\left(\nabla^2 u\right)^2 + b\left(\nabla\dot{u}\right)^2\right] + c\nabla\theta\cdot\nabla\dot{u}, \tag{3.7.9}$$

which is completely different from the definition of $\mathcal{P}^i_m$ given in (3.7.1). Consequently, the local form (3.7.3) of the new formulation of the first law (3.7.4) is expressed by

$$\rho\dot{e} = \frac{1}{2}\frac{d}{dt}\left[a\left(\nabla^2 u\right)^2 + b\left(\nabla\dot{u}\right)^2\right] + c\nabla\theta\cdot\nabla\dot{u} + \rho h. \tag{3.7.10}$$

Moreover, by virtue of (3.7.2) and putting

$$\mathbf{N}' = \left[a\nabla\left(\nabla^2 u\right) - b\nabla\ddot{u} - c\nabla\theta\right]\dot{u} - a\nabla^2 u\,\nabla\dot{u}, \tag{3.7.11}$$

we derive the expression for the external mechanical power

$$\tilde{\mathcal{P}}^e_m = -\nabla\cdot\mathbf{N}' + \rho f\dot{u}.$$

It is now possible to better understand the difference between the new formulation and the classical one, proposed by Truesdell and Noll [313] and Coleman [67] (also [311]) for simple materials, in which the first law relating to mechanical systems is expressed by (see (3.3.7))

$$\rho\dot{e} = \mathbf{T}\cdot\mathbf{L} - \nabla\cdot\mathbf{q} + \rho r. \tag{3.7.12}$$

This expression clearly agrees with the representation (3.7.3) when the internal power $\tilde{\mathcal{P}}^i_m$ has the form (3.7.1) and h, by virtue of the balance equation for heat (see (3.1.3)), is given by

$$\rho h = -\nabla\cdot\mathbf{q} + \rho r. \tag{3.7.13}$$

The representation (3.7.12) does not hold for nonsimple materials. In fact, already in the example of the plate, we have seen that (3.7.10), deduced from (3.7.4) with $\tilde{\mathcal{P}}^i$ defined by (3.7.9) and h given by (3.7.13), is not compatible with (3.7.12), where $\mathbf{T}$ is expressed by (3.7.5). Therefore, (3.7.12) must be modified.

Dunn and Serrin [97], but subsequently also Fabrizio and Morro [122], have proposed a modification of (3.7.12), by assuming

$$\rho\dot{e} = \mathbf{T}\cdot\mathbf{L} - \nabla\cdot\mathbf{N} - \nabla\cdot\mathbf{q} + \rho r, \tag{3.7.14}$$

where the vector $\mathbf{N}$ is a suitable extra flux.

For the example of the plate, we firstly observe that using (3.7.8) and (3.7.11), we can eliminate in (3.7.10) the expression for $\tilde{\mathcal{P}}^i_m$ given by (3.7.9), thus obtaining

$$\rho\dot{e} = -\frac{d}{dt}T + \rho f\dot{u} - \nabla\cdot\mathbf{N}' + \rho h; \tag{3.7.15}$$

hence, taking into account (3.7.7) and (3.7.13), we also have

$$\rho\dot{e} = \mathbf{T}\cdot\nabla\dot{u} - \nabla\cdot(\mathbf{T}\dot{u} + \mathbf{N}') - \nabla\cdot\mathbf{q} + \rho r, \tag{3.7.16}$$

that is, (3.7.14) is satisfied with $\mathbf{N}$ expressed by

$$\mathbf{N} \equiv (\mathbf{T}\dot{u} + \mathbf{N}') = -a\nabla^2 u\,\nabla\dot{u},$$

by virtue of (3.7.5) and again of (3.7.11).

An analogous problem arises when we consider a thermoelastic plate with memory characterized by the following constitutive equations:

$$\begin{aligned} \mathbf{T}(\mathbf{x},t) &= -\nabla\left[\int_0^\infty C'(s)\nabla^2 u^t(\mathbf{x},s)ds - C_0\nabla^2 u(\mathbf{x},t)\right] + c\nabla\theta(\mathbf{x},t), \\ e(\mathbf{x},t) &= \tilde{e}(\theta(\mathbf{x},t), \nabla^2 u(\mathbf{x},t), \nabla^2 u^t(\mathbf{x},s)), \\ \mathbf{q}(\mathbf{x},t) &= -k_0\nabla\theta(\mathbf{x},t), \end{aligned} \tag{3.7.17}$$

where the scalar kernel $C'(\cdot)$ is a suitable smooth function.

From the equation of motion (3.7.6), we have already derived the balance equation of the mechanical power (3.7.7), where, using $(3.7.17)_1$, we obtain

$$\begin{aligned} -\mathbf{T}\cdot\nabla\dot{u} &= \left\{\nabla\left[\int_0^\infty C'(s)\nabla^2 u^t(s)ds - C_0\nabla^2 u\right] - c\nabla\theta\right\}\cdot\nabla\dot{u} \\ &= \nabla\cdot\left\{\left[\int_0^\infty C'(s)\nabla^2 u^t(s)ds - C_0\nabla^2 u - c\theta\right]\nabla\dot{u}\right\} \\ &\quad - \int_0^\infty C'(s)\nabla^2 u^t(s)ds\nabla^2\dot{u} + \frac{C_0}{2}\frac{d}{dt}\left(\nabla^2 u\right)^2 + c\theta\nabla^2\dot{u}. \end{aligned}$$

Thus, (3.7.7) yields

$$\begin{aligned}\frac{d}{dt}\left(\frac{1}{2}\rho\dot{u}^2\right)&+\int_0^\infty C'(s)\nabla^2u^t(s)ds\nabla^2\dot{u}-\frac{C_0}{2}\frac{d}{dt}\left(\nabla^2u\right)^2-c\theta\nabla^2\dot{u}\\&=\nabla\cdot\left(\left\{-\nabla\left[\int_0^\infty C'(s)\nabla^2u^t(s)ds-C_0\nabla^2u\right]+c\nabla\theta\right\}\dot{u}\right.\\&\quad\left.+\left[\int_0^\infty C'(s)\nabla^2u^t(s)ds-C_0\nabla^2u-c\theta\right]\nabla\dot{u}\right)+\rho f\dot{u}.\end{aligned}$$

Hence, it follows that

$$\tilde{\mathcal{P}}^i_m=\int_0^\infty C'(s)\nabla^2u^t(s)ds\nabla^2\dot{u}-\frac{C_0}{2}\frac{d}{dt}\left(\nabla^2u\right)^2-c\theta\nabla^2\dot{u}.$$

Using (3.7.3), we can give an expression for the thermal power as follows:

$$\rho h=\rho\dot{e}-\tilde{\mathcal{P}}^i_m=\rho\dot{e}-\int_0^\infty C'(s)\nabla^2u^t(s)ds\nabla^2\dot{u}+\frac{C_0}{2}\frac{d}{dt}\left(\nabla^2u\right)^2+c\theta\nabla^2\dot{u}.$$

To obtain the expression (3.7.14), we put

$$\begin{aligned}\mathbf{N}'=&\left\{\nabla\left[\int_0^\infty C'(s)\nabla^2u^t(s)ds-C_0\nabla^2u\right]-c\nabla\theta\right\}\dot{u}\\&-\left[\int_0^\infty C'(s)\nabla^2u^t(s)ds-C_0\nabla^2u-c\theta\right]\nabla\dot{u},\end{aligned}\tag{3.7.18}$$

instead of (3.7.11). Relations (3.7.15) and (3.7.16) follow, where by virtue of $(3.7.17)_1$ and (3.7.18), the quantity $\mathbf{N}$ is now given by

$$\mathbf{N}=\mathbf{T}\dot{u}+\mathbf{N}'=-\left[\int_0^\infty C'(s)\nabla^2u^t(s)ds-C_0\nabla^2u-c\theta\right]\nabla\dot{u}.$$

Other interesting examples, for which the classical representation of the power, used in the first law, does not coincide with that following from a correct balance between the internal and external powers, occur in electromagnetism, in the study of phase transitions, and also in other physical systems, such as those describing processes of phase separation, for example, by means of the Cahn–Hilliard equation [44]. This topic is discussed below.

A further interesting application relates to the thermodynamics of superconducting materials. It has been shown in [122] that for these materials, an extra flux must be introduced into the first law, which is proportional to the superconducting current.

The case of electromagnetism is discussed in Chap. 6.

As a final example of nonsimple materials, we consider the thermodynamics of phase transitions in a binary mixture, characterized by the Cahn–Hilliard equation

$$\dot{c}=\nabla\cdot\mathbf{J},\tag{3.7.19}$$

where $\mathbf{J}$ is the mass flux given by

$$\mathbf{J}=M(c)\nabla\mu(c).\tag{3.7.20}$$

Here c denotes the concentration of one of the two components, with a range of values in the interval $[0, 1]$. The quantity $M(c)$ is the *mobility*, representing the density with which the two phases are mixed, and is such that

$$M(0) = M(1) = 0,$$

while the *chemical potential* $\mu(c)$ is given by

$$\mu(c) = -\gamma\nabla^2 c + \theta G'(c) + \theta_0 F'(c), \qquad \gamma > 0. \tag{3.7.21}$$

Here, θ_0 is the transition temperature, while $G(c)$ and $F(c)$ are assigned the polynomial forms

$$G(c) = \beta\frac{c^2}{2}, \quad F(c) = \beta\left(\frac{c^4}{4} - \frac{c^2}{2}\right), \qquad \beta > 0,$$

corresponding to a second-order transition as described by the Cahn–Hilliard equation.

From (3.7.19) and (3.7.20), we have

$$\dot{c} = \nabla \cdot [M(c)\nabla\mu(c)], \tag{3.7.22}$$

whence, using (3.7.21), we obtain

$$\dot{c} = \nabla \cdot \left\{M(c)\nabla\left[\theta_0 F'(c) + \theta G'(c) - \gamma\nabla^2 c\right]\right\}.$$

This equation must be related to the heat equation, derived from the energy balance law

$$\dot{e} = \tilde{\mathcal{P}}^i_c + h, \tag{3.7.23}$$

where $\tilde{\mathcal{P}}^i_c$ is the internal power of the mixture. Multiplying (3.7.22) by the potential $\mu(c)$, we have the equation for the power

$$\dot{c}\mu(c) = \nabla \cdot [M(c)\mu(c)\nabla\mu(c)] - M(c)[\nabla\mu(c)]^2.$$

Using (3.7.21) again, we obtain

$$\theta_0\dot{F}(c) + \theta\dot{G}(c) + \frac{\gamma}{2}\frac{d}{dt}(\nabla c)^2 + M(c)[\nabla\mu(c)]^2 = \nabla \cdot [\gamma\dot{c}\nabla c + M(c)\mu(c)\nabla\mu(c)].$$

Thus, the power $\tilde{\mathcal{P}}^i_c$ is expressed by

$$\tilde{\mathcal{P}}^i_c = \theta_0\dot{F}(c) + \theta\dot{G}(c) + \frac{\gamma}{2}\frac{d}{dt}(\nabla c)^2 + M(c)\,[\nabla\mu(c)]^2.$$

By assuming for e the form

$$e = \theta_0 F(c) + \frac{\gamma}{2}(\nabla c)^2 + \tilde{e}(\theta),$$

Eq. (3.7.23) becomes

$$\tilde{e}_\theta\theta_t = \theta\dot{G}(c) + M(c)\,[\nabla\mu(c)]^2 - \nabla \cdot \mathbf{q} + r,$$

with the aid of (3.7.13).

3.7.2 Second Law of Thermodynamics

For simple materials, the second law is expressed by the Clausius–Duhem inequality, which assumes the form (3.4.11), i.e.,

$$\rho\dot{\eta} \geq -\nabla \cdot \frac{\mathbf{q}}{\theta} + \rho\frac{r}{\theta}, \tag{3.7.24}$$

where η denotes the entropy function and r the heat supply.

In 1967, I. Müller [268] proposed a new version of this inequality by replacing (3.7.24) with the more general expression

$$\rho\dot{\eta} \geq -\nabla \cdot \boldsymbol{\Phi} + \rho\frac{r}{\theta}, \tag{3.7.25}$$

where the vector $\boldsymbol{\Phi}$, the *entropy flux*, is characterized by a constitutive equation. If we assume for $\boldsymbol{\Phi}$ the form

$$\boldsymbol{\Phi} = \frac{\mathbf{q}}{\theta} + \boldsymbol{\Phi}',$$

where $\boldsymbol{\Phi}'$ denotes an *entropy extra flux*, (3.7.25) can be written as

$$\rho\dot{\eta} \geq -\nabla \cdot \frac{\mathbf{q}}{\theta} - \nabla \cdot \boldsymbol{\Phi}' + \rho\frac{r}{\theta}. \tag{3.7.26}$$

In order to better understand the difference between simple and nonsimple materials, let us derive the balance law of entropy power. If the heat equation (3.7.13) is divided by the absolute temperature θ, we obtain the identity

$$\rho\frac{h}{\theta} + \frac{1}{\theta^2}\mathbf{q} \cdot \nabla\theta = -\nabla \cdot \frac{\mathbf{q}}{\theta} + \rho\frac{r}{\theta}, \tag{3.7.27}$$

which is the desired relation. For a simple material, we can claim that the internal entropy power is defined by

$$\mathcal{P}^i_\eta := \rho\frac{h}{\theta} + \frac{1}{\theta^2}\mathbf{q} \cdot \nabla\theta, \tag{3.7.28}$$

while the external entropy power is given by

$$\mathcal{P}^e_\eta := -\nabla \cdot \frac{\mathbf{q}}{\theta} + \rho\frac{r}{\theta}.$$

Thus, by (3.7.27), we see that the formulation (3.7.24), relating to simple materials, reduces to the inequality

$$\rho\dot{\eta} \geq \mathcal{P}^i_\eta = \rho\frac{h}{\theta} + \frac{1}{\theta^2}\mathbf{q} \cdot \nabla\theta. \tag{3.7.29}$$

In general, for nonsimple materials, the internal entropy power is not given by (3.7.28). Using (3.7.27) again, the inequality (3.7.26) becomes

$$\rho\dot{\eta} \geq \rho\frac{h}{\theta} + \frac{1}{\theta^2}\mathbf{q} \cdot \nabla\theta - \nabla \cdot \boldsymbol{\Phi}'. \tag{3.7.30}$$

From the inequalities (3.7.24) and (3.7.26) (or (3.7.29) and (3.7.30)), we see that the second law assumes different expressions for simple and nonsimple materials. Following [75], we propose the second law in a unique general form as follows.

• **Second principle of thermodynamics** (on cycles). *For any cyclic process* (σ^i, P), *i.e.*, $\hat{\rho}(\sigma^i, P) = \sigma^i$, *the internal entropy power* $\tilde{\mathfrak{P}}^i_\eta$ *satisfies the inequality*

$$\oint \tilde{\mathfrak{P}}^i_\eta(\sigma(t), P(t))dt \leq 0, \tag{3.7.31}$$

where $\sigma(t) = \hat{\rho}(\sigma^i, P_t)$.

By a similar argument to that used in the context of (3.4.11), we can prove that from (3.7.31) there exists the entropy function $\eta(\sigma)$ such that

$$\rho\dot{\eta}(\sigma) \geq \tilde{\mathfrak{P}}^i_\eta(\sigma, P), \tag{3.7.32}$$

so that we recover (3.7.30) on putting

$$\tilde{\mathfrak{P}}^i_\eta = \rho\frac{h}{\theta} + \frac{1}{\theta^2}\mathbf{q}\cdot\nabla\theta - \nabla\cdot\mathbf{\Phi}'. \tag{3.7.33}$$

We prefer to state the second law by the inequality (3.7.31) or (3.7.32), since the representation (3.7.30) of the second law is ambiguous, because of the term $\nabla\cdot\mathbf{\Phi}'$.* In order to understand the natural expression for the second law by means of internal entropy power $\tilde{\mathfrak{P}}^i_\eta$ used in (3.7.31) and (3.7.32), let us introduce the example considered in the work of Cimmelli and Frischmuth [66], in which they have studied the thermodynamics of the model proposed by Guyer and Krumhansl [193] for the heat flux, characterized by the constitutive law

$$\dot{\mathbf{q}} + \frac{1}{\tau_R}\mathbf{q} = -c_V\nabla\theta + \tau_N\left[\nabla^2\mathbf{q} + 2\nabla(\nabla\cdot\mathbf{q})\right], \quad \tau_R > 0,\ \tau_N > 0. \tag{3.7.34}$$

For this equation, when the coefficient c_V has the form

$$c_V = \frac{c_0}{\theta^2}, \quad c_0 > 0, \tag{3.7.35}$$

an entropy extra flux can be introduced.

To derive the balance equation (3.7.27), we consider the inner product of (3.7.34) by $\mathbf{q}$, taking account of (3.7.35); thus, we obtain the quantity $\frac{1}{\theta^2}\mathbf{q}\cdot\nabla\theta$, which allows us to rewrite (3.7.27) as

$$\begin{aligned}\rho\frac{h}{\theta} - \frac{1}{2c_0}\frac{d}{dt}\mathbf{q}^2 - \frac{1}{c_0\tau_R}\mathbf{q}^2 - \frac{\tau_N}{c_0}\left[(\nabla\mathbf{q})^2 + 2(\nabla\cdot\mathbf{q})^2\right]& \\ = -\nabla\cdot\frac{\mathbf{q}}{\theta} + \rho\frac{r}{\theta} - \frac{\tau_N}{c_0}\nabla\cdot[(\nabla\mathbf{q})\,\mathbf{q} + 2(\nabla\cdot\mathbf{q})\,\mathbf{q}&.\end{aligned} \tag{3.7.36}$$

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* In the literature, examples for which it is necessary to introduce an entropy extra flux $\mathbf{\Phi}'$ are very few. Only materials for which there is a nonlocal constitutive equation for the heat flux $\mathbf{q}$ have need of an extra flux in (3.7.26) or in (3.7.30). It has been shown (see [122, Chapter 11.2]) that for isothermal processes, the introduction of an energy extra flux in the first law is equivalent to the inclusion of an entropy extra flux in the second law. But this equivalence holds only for isothermal processes.

Hence, it follows that the expression of $\tilde{\mathcal{P}}^i_\eta$ considered in (3.7.32) is given by

$$\tilde{\mathcal{P}}^i_\eta = \rho\frac{h}{\theta} - \frac{1}{2c_0}\frac{d}{dt}\mathbf{q}^2 - \frac{1}{c_0\tau_R}\mathbf{q}^2 - \frac{\tau_N}{c_0}\left[(\nabla\mathbf{q})^2 + 2(\nabla\cdot\mathbf{q})^2\right], \tag{3.7.37}$$

while the external entropy power has the form

$$\tilde{\mathcal{P}}^e_\eta = -\nabla\cdot\frac{\mathbf{q}}{\theta} + \rho\frac{r}{\theta} - \nabla\cdot\mathbf{\Phi}'_0, \tag{3.7.38}$$

where we have put

$$\mathbf{\Phi}'_0 = \frac{\tau_N}{c_0}[(\nabla\mathbf{q})\,\mathbf{q} + 2(\nabla\cdot\mathbf{q})\,\mathbf{q}]. \tag{3.7.39}$$

Finally, from (3.7.32), using (3.7.36)–(3.7.38), we have

$$\rho\dot{\eta} \geq \tilde{\mathcal{P}}^i_\eta \equiv \tilde{\mathcal{P}}^e_\eta = -\nabla\cdot\frac{\mathbf{q}}{\theta} + \rho\frac{r}{\theta} - \nabla\cdot\mathbf{\Phi}'_0,$$

that is, (3.7.30) is satisfied with the entropy extra flux (3.7.39).

However, the natural form of the second law is the representation (3.7.32) with the expression (3.7.37) for $\tilde{\mathcal{P}}^i_\eta$.

Remark 3.7.1. Further examples of nonsimple materials are discussed in some detail in Chap. 21. These include second-gradient thermoviscoelastic fluids and heat flow in a rigid conductor, with nonlocal behavior and thermal memory. The rigid conductor problem is related to the material associated with (3.7.34). A general theory of nonsimple or nonlocal materials is also proposed. The main emphasis in that chapter is to introduce generalizations of some of the free energy functionals discussed in Chaps. 10 and 11 for simple materials.