

4.5 Balance of Energy in Continuum Thermodynamics

In this section we consider both *mechanical* and *thermal* energy which are essential in many problems of physics and engineering. The effect of other energies (such as electric, chemical ...) on the behavior of a continuum is a topic beyond the scope of this text.

In a thermodynamic context the conservation of mass and the momentum balance principles are supplemented by the balance of energy and the entropy inequality law. The development of the concepts of energy and entropy has been one of the most important achievements in the evolution of physics. For an extensive account of these concepts see, for example, TRUESDELL and TOUPIN [1960, Chapter E], the two-volume work of KESTIN [1979], or ŠILHAVÝ [1997] and WILMAŃSKI [1998].

In this section we discuss briefly the balance of energy equation in a thermodynamic context. To begin with, we introduce some important terminology common in thermodynamics.

General notation. A continuum which possesses both mechanical and thermal energy is called a **thermodynamic continuum**. We say that the **thermodynamic state** or the **condition** of a system is known if all quantities throughout the entire system are known. All quantities characterizing a system at a certain state are called **thermodynamic state variables**. They are macroscopic quantities and, in general, they depend on *position* and *time*. For example, the thermodynamic state of a thermoelastic solid can be represented in a seven-dimensional state space with six variables corresponding to the strains and one to temperature. The function that describes a certain state variable is called a **thermodynamic state function**. Any equation that interrelates state variables is called **equation of state** or **constitutive equation**.

Any change that a system undergoes from one thermodynamic state to another is called a **thermodynamic process**. The path that connects the two states is parameterized by time t . If a system returns to its initial state at the end of a thermodynamic process this system is said to have undergone a so-called **cycle** (initial and final states are identical).

A **non-equilibrium state** is a state of imbalance (there exists a gradient of temperature and velocity), while an **equilibrium state** is a state of balance (of uniform temperature and zero velocity). To study non-equilibrium or equilibrium states is a central goal of continuum thermodynamics.

A system within equilibrium has no tendency to change when it is isolated from its surroundings. If there is no change in the values of the state variables at any particle of the system with time we say that this system is in **thermodynamic equilibrium** or **thermal equilibrium**. The transition from one state of thermodynamic equilibrium to another is studied in **thermostatics**. A process in a system that remains close to a state

of thermodynamic equilibrium at each time is referred to as a **quasi-static process** or **quasi-equilibrium process**. A quasi-static process is a sufficiently slow process whereby enough time remains for the system to adjust itself internally. It is basically a process during which the system is in equilibrium at all times; the contributions due to dynamical quantities are negligible.

Heat is the form of (thermal) energy that is transferred between a system and its surroundings (or between two systems) by virtue of a temperature gradient. The term '*heat*' is understood to mean **heat transfer** in thermodynamics.

Thermal power. Let the **thermal (non-mechanical) power** or the **rate of thermal work** be denoted by \mathcal{Q} and defined by

$$\mathcal{Q}(t) = \int_{\partial\Omega} q_n ds + \int_{\Omega} r dv = \int_{\partial\Omega_0} Q_N dS + \int_{\Omega_0} R dV , \quad (4.118)$$

which is represented in the spatial and material descriptions, respectively.

The time-dependent scalar functions q_n and Q_N denote **heat fluxes**, determining heat per unit time and per unit current and reference surface area, respectively. The total heat fluxes $\int_{\partial\Omega} q_n ds$ and $\int_{\partial\Omega_0} Q_N dS$ measure the rate at which heat *enters* (inward normal flux) the body across the current and the reference boundary surfaces $\partial\Omega$ and $\partial\Omega_0$, respectively.

The time-dependent scalar fields $r = r(\mathbf{x}, t)$ and $R = R(\mathbf{X}, t)$ in eq. (4.118) denote **heat sources** per unit time and per unit current and reference volume, respectively (see Figure 4.3). A heat source is a reservoir that supplies energy in the form of heat. The total heat sources $\int_{\Omega} r dv$ and $\int_{\Omega_0} R dV$ measure the rate at which heat is generated (or destroyed) into a certain region of a body.

The counterpart of Cauchy's stress theorem (3.3) in continuum mechanics is the **Stokes' heat flux theorem** in thermodynamics. It postulates that the scalar functions q_n and Q_N are linear functions of the outward unit normals so that

$$\left. \begin{aligned} q_n(\mathbf{x}, t, \mathbf{n}) &= -\mathbf{q}(\mathbf{x}, t) \cdot \mathbf{n} & \text{or} & \quad q_n = -q_a n_a , \\ Q_N(\mathbf{X}, t, \mathbf{N}) &= -\mathbf{Q}(\mathbf{X}, t) \cdot \mathbf{N} & \text{or} & \quad Q_N = -Q_A N_A . \end{aligned} \right\} \quad (4.119)$$

The time-dependent spatial vector field $\mathbf{q} = \mathbf{q}(\mathbf{x}, t)$ is the so-called **Cauchy heat flux** (or **true heat flux**) defined per unit surface area in Ω , and \mathbf{n} is the *outward* unit normal to an infinitesimal spatial surface element $ds \in \partial\Omega$ at the current position \mathbf{x} . The **Piola-Kirchhoff heat flux** (or **nominal heat flux**) and the *outward* unit normal to an infinitesimal material surface element $dS \in \partial\Omega_0$ at \mathbf{X} are denoted by the vectors $\mathbf{Q} = \mathbf{Q}(\mathbf{X}, t)$ and \mathbf{N} , respectively. The time-dependent material vector field \mathbf{Q} determines the heat flux per unit surface area in Ω_0 .

The negative signs in eqs. (4.119) are needed (see Figure 4.3) because the unit vectors \mathbf{n} and \mathbf{N} are outward normals to $\partial\Omega$ and $\partial\Omega_0$, respectively. However, we claim in (4.118) that heat enters the body (inward normal flux).

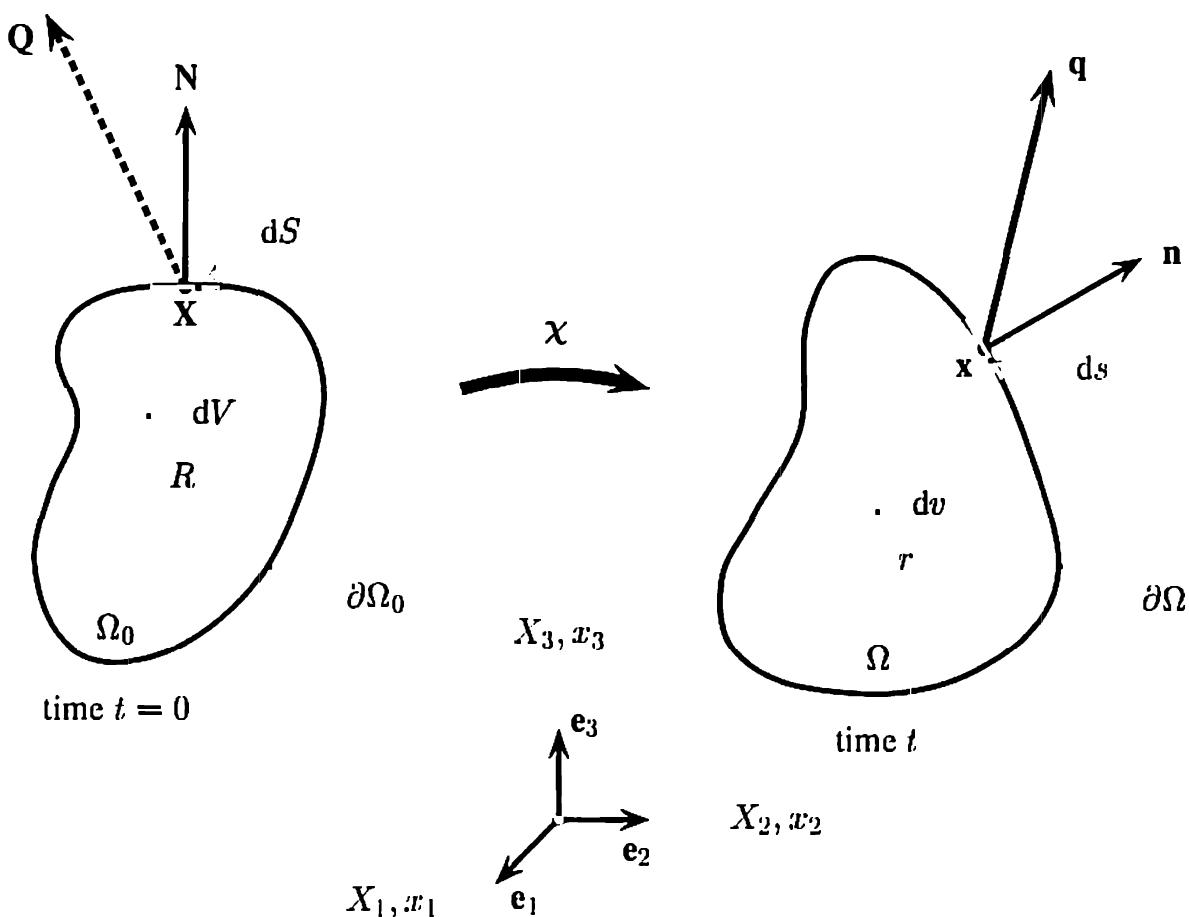


Figure 4.3 Heat flux vectors \mathbf{q} , \mathbf{Q} and heat sources r , R .

In order to relate the contravariant vectors \mathbf{q} and \mathbf{Q} to one another, we equate the total heat fluxes $\int_{\partial\Omega_0} Q_N dS$ and $\int_{\partial\Omega} q_n ds$. Hence, with the fundamental Stokes' heat flux theorem (4.119), Nanson's formula (2.54) and manipulations according to (1.95) we obtain

$$\begin{aligned} \int_{\partial\Omega_0} \mathbf{Q} \cdot \mathbf{N} dS &= \int_{\partial\Omega} \mathbf{q} \cdot \mathbf{n} ds = \int_{\partial\Omega_0} \mathbf{q} \cdot J \mathbf{F}^{-T} \mathbf{N} dS \\ &= \int_{\partial\Omega_0} J \mathbf{F}^{-1} \mathbf{q} \cdot \mathbf{N} dS . \end{aligned} \quad (4.120)$$

Comparing the left and right-hand sides of (4.120) we conclude that the Piola-Kirchhoff heat flux \mathbf{Q} may be related to the Cauchy heat flux \mathbf{q} . We have, by analogy with (3.8),

$$\mathbf{Q} = J \mathbf{F}^{-1} \mathbf{q} = J \chi_*^{-1} (\mathbf{q}^\sharp) \quad \text{or} \quad Q_A = J F_{Aa}^{-1} q_a , \quad (4.121)$$

which may be viewed as the pull-back operation on the contravariant vector \mathbf{q}^\sharp by the inverse motion χ_*^{-1} scaled by the volume ratio J . Such a transformation we called the *Piola transformation*, here relating the heat flux vectors \mathbf{Q} and \mathbf{q} (compare with the definition on p. 84).

First law of thermodynamics in spatial description. Here we consider the case in which thermal power is added to a thermodynamic continuum. Thus, the rate of work done on the continuum body, i.e. the sum of the rate of internal *mechanical* work \mathcal{P}_{int} and the rate of *thermal* work \mathcal{Q} , equals the rate of internal energy \mathcal{E} . Consequently, eq. (4.92) becomes

$$\mathcal{P}_{\text{int}}(t) + \mathcal{Q}(t) = \frac{D}{Dt}\mathcal{E}(t) , \quad (4.122)$$

which is often referred to as the **balance of thermal energy**.

By substituting eq. (4.122) into (4.85) we deduce the important identity, namely

$$\boxed{\frac{D}{Dt}\mathcal{K}(t) + \frac{D}{Dt}\mathcal{E}(t) = \mathcal{P}_{\text{ext}}(t) + \mathcal{Q}(t)} \quad (4.123)$$

Using the explicit expressions for \mathcal{K} , \mathcal{E} , which are given by eqs. (4.83), (4.91), and for \mathcal{P}_{ext} , \mathcal{Q} , which are given by eqs. (4.82), (4.118)₁, we may write the global form

$$\frac{D}{Dt} \int_{\Omega} \left(\frac{1}{2} \rho \mathbf{v}^2 + e_c \right) dv = \int_{\partial\Omega} (\mathbf{t} \cdot \mathbf{v} + q_n) ds + \int_{\Omega} (\mathbf{b} \cdot \mathbf{v} + r) dv . \quad (4.124)$$

It is a thermodynamic extension of eq. (4.94) and postulates **balance of energy** (mechanical and thermal), a fundamental axiom in mechanics, known as the **first law of thermodynamics**. In particular, eq. (4.124) is the first law of thermodynamics in the spatial description.

It states that the rate of change of total energy (kinetic \mathcal{K} and internal energy \mathcal{E}) of a thermodynamic system equals the rate at which external mechanical work (external mechanical power) \mathcal{P}_{ext} is done on that system by surface tractions and body forces plus the rate at which thermal work \mathcal{Q} is done by heat fluxes and heat sources. The first law of thermodynamics governs the transformation from one type of energy involved in a thermodynamic process into another, but it *never* governs the direction of that energy transfer.

In order to express eq. (4.122) more explicitly we rewrite the thermal power \mathcal{Q} first, i.e. (4.118)₁. By means of the Stokes' heat flux theorem (4.119)₁ and the divergence theorem according to eq. (1.293), we may deduce that $\mathcal{Q}(t) = \int_{\Omega} (-\text{div} \mathbf{q} + r) dv$. By recalling the rate of internal mechanical work \mathcal{P}_{int} and the internal energy \mathcal{E} from eqs. (4.84)₁ and (4.91), we obtain

$$\frac{D}{Dt} \int_{\Omega} e_c dv = \int_{\Omega} (\boldsymbol{\sigma} : \mathbf{d} - \text{div} \mathbf{q} + r) dv , \quad (4.125)$$

which is a reduced global form of balance of energy (4.124) in the spatial description.

First law of thermodynamics in material description. In order to rewrite balance of energy (4.124) in terms of material coordinates, we recall the equivalent forms of the total energy, the external mechanical power \mathcal{P}_{ext} and the thermal power Q , that are given by eqs. (4.95), (4.105), and (4.82), (4.98) and (4.118), respectively.

Thus, the first law of thermodynamics in the material description reads

$$\frac{D}{Dt} \int_{\Omega_0} \left(\frac{1}{2} \rho_0 \mathbf{V}^2 + e \right) dV = \int_{\partial\Omega_0} (\mathbf{T} \cdot \mathbf{V} + Q_N) dS + \int_{\Omega_0} (\mathbf{B} \cdot \mathbf{V} + R) dV . \quad (4.126)$$

Following arguments analogous to those which led to (4.125), we find the reduced global form of balance of energy in the material description, i.e.

$$\frac{D}{Dt} \int_{\Omega_0} e dV = \int_{\Omega_0} (\mathbf{P} : \dot{\mathbf{F}} - \text{Div} \mathbf{Q} + R) dV . \quad (4.127)$$

In order to achieve the local form we must rewrite the term on the left-hand side of eq. (4.127). Since the reference volume V is independent of time we may write $D/Dt \int_{\Omega_0} e dV = \int_{\Omega_0} \dot{e} dV$. Note that the volume is arbitrary, leading to the local form of the balance of energy in the material description

$$\dot{e} = \mathbf{P} : \dot{\mathbf{F}} - \text{Div} \mathbf{Q} + R \quad \text{or} \quad \dot{e} = P_{aA} \dot{F}_{aA} - \frac{\partial Q_A}{\partial X_A} + R , \quad (4.128)$$

presented in symbolic and index notation, respectively.

The first-order partial differential equation is due to *Kirchhoff* and holds at any particle of the body for all times.

EXERCISES

1. Assume a continuum body not subjected to body forces and heat sources. Establish the balance equations

$$\frac{D}{Dt} \int_{\Omega} \left(\frac{1}{2} \rho \mathbf{v}^2 + e_c \right) dV = \int_{\partial\Omega} (\boldsymbol{\sigma} \mathbf{v} - \mathbf{q}) \cdot \mathbf{n} dS ,$$

$$\frac{D}{Dt} \int_{\Omega_0} \left(\frac{1}{2} \rho_0 \mathbf{V}^2 + e \right) dV = \int_{\partial\Omega_0} (\mathbf{P}^T \mathbf{V} - \mathbf{Q}) \cdot \mathbf{N} dS .$$

These relations equate the rate of change of the total energy of a continuum body occupying a certain region with the total flux out of the boundary surfaces of that region. The vectors $\boldsymbol{\sigma} \mathbf{v} - \mathbf{q}$ and $\mathbf{P}^T \mathbf{V} - \mathbf{Q}$ are often referred to as the **energy flux vectors** with respect to the current and reference configurations, respectively.

2. Starting from (4.124), show that the local spatial form of the balance equation has the form

$$\frac{\partial}{\partial t} \left(\frac{1}{2} \rho \mathbf{v}^2 + e_c \right) = \operatorname{div} [\sigma \mathbf{v} - \mathbf{q} - (\frac{1}{2} \rho \mathbf{v}^2 + e_c) \mathbf{v}] + \mathbf{b} \cdot \mathbf{v} + r \quad .$$

Hint: Use eqs. (2.50), (2.25), (2.175)₆ and the rule according to (1.287) for the left-hand side of (4.124).

3. Derive the local form of the balance equation in the spatial description corresponding to eq. (4.128) and note that we have used the internal energy per unit *volume* rather than per unit *mass* (see eq. (4.91)).

4.6 Entropy Inequality Principle

The first law of thermodynamics governs the energy transfer within a thermodynamic process, but is insensitive to the direction of the energy transfer. In the following we derive a much finer principle, that is the second law of thermodynamics, which is responsible for the direction of an energy transfer process. We introduce the concept of entropy and discuss some of the consequences of the second law of thermodynamics.

Second law of thermodynamics. Physical observations show that heat always flows from the warmer to the colder region of a body (free from sources of heat), *not vice versa*; mechanical energy can be transformed into heat by friction, and this can never be converted back into mechanical energy.

We introduce a fundamental state variable, the **entropy** (coming from the Greek words *ἐν* and *τρόπος* meaning ‘in’ and ‘turning, direction’, respectively). It is an important thermodynamic property first described in the works of *Clausius* in the second half of the nineteenth century. The entropy can be viewed as the quantitative measure of microscopic randomness and disorder (see, for example, CALLEN [1985, Chapter 17]). A physical interpretation is provided by the subject of *statistical mechanics*. For a more detailed physical interpretation the reader is referred to Section 7.1 of this text. We introduce the notations $\eta_c = \eta_c(\mathbf{x}, t)$ and $\eta = \eta(\mathbf{X}, t)$ for the entropy per unit current and reference volume, respectively, at a certain point and time t . In other texts the entropy is frequently designated by s or S .

The entropy possessed by a continuum body occupying a certain region, denoted by \mathcal{S} , is defined to be

$$\mathcal{S}(t) = \int_{\Omega} \eta_c(\mathbf{x}, t) d\mathbf{v} = \int_{\Omega_0} \eta(\mathbf{X}, t) dV \quad , \quad (4.129)$$

with $\eta(\mathbf{X}, t) = J(\mathbf{X}, t)\eta_c(\mathbf{x}, t)$, which should be compared with the analogues of (4.103) and (4.104), respectively. This definition is commonly introduced in continuum mechanics and differs from the definitions used in statistical mechanics.

Let the **rate of entropy input** into a certain region of a continuum body consist of the value of entropy transferred across its boundary surface and the entropy generated (or destroyed) inside that region. We denote it by \tilde{Q} and write

$$\tilde{Q}(t) = - \int_{\partial\Omega} \mathbf{h} \cdot \mathbf{n} ds + \int_{\Omega} \tilde{r} dv = - \int_{\partial\Omega_0} \mathbf{H} \cdot \mathbf{N} dS + \int_{\Omega_0} \tilde{R} dV . \quad (4.130)$$

The time-dependent scalar fields $\tilde{r} = \tilde{r}(\mathbf{x}, t)$ and $\tilde{R} = \tilde{R}(\mathbf{X}, t)$ denote **entropy sources** per unit time and per unit current and reference volume, respectively. The total entropy sources $\int_{\Omega} \tilde{r} dv$ and $\int_{\Omega_0} \tilde{R} dV$ measure the rate at which entropy is generated (or destroyed) into a region of a body. The time-dependent vector fields $\mathbf{h} = \mathbf{h}(\mathbf{x}, t)$ and $\mathbf{H} = \mathbf{H}(\mathbf{X}, t)$ determine the **Cauchy entropy flux** (or **true entropy flux**) defined per unit current surface area in Ω and the **Piola-Kirchhoff entropy flux** (or **nominal entropy flux**) per unit reference surface area in Ω_0 , respectively.

As usual, the outward unit normals to the infinitesimal surface elements $ds \in \partial\Omega$ at \mathbf{x} and $dS \in \partial\Omega_0$ at \mathbf{X} are denoted by \mathbf{n} and \mathbf{N} , respectively. Since we have defined the unit vectors \mathbf{n} and \mathbf{N} to be *outward* normals to $\partial\Omega$ and $\partial\Omega_0$ and since we compute the rate of entropy *input* (entropy entering the body), we need the negative signs in relation (4.130).

The difference between the rate of change of entropy \dot{S} and the rate of entropy input \tilde{Q} into a body determines the **total production of entropy** per unit time, which we denote by Γ . We postulate that the total entropy production for all thermodynamic processes is never negative, following the mathematical expression

$$\Gamma(t) = \frac{D}{Dt} S(t) - \tilde{Q}(t) \geq 0 , \quad (4.131)$$

which is known as the **second law of thermodynamics**. Unlike the considerations in previous sections, it is an inequality rather than an equation often referred to as the **entropy inequality principle**.

More explicitly, with eqs. (4.129)₁ and (4.130)₁ we find from (4.131) the global spatial form of the second law of thermodynamics in the notation of continuum mechanics, i.e.

$$\Gamma(t) = \frac{D}{Dt} \int_{\Omega} \eta_c(\mathbf{x}, t) dv + \int_{\partial\Omega} \mathbf{h} \cdot \mathbf{n} ds - \int_{\Omega} \tilde{r} dv \geq 0 . \quad (4.132)$$

These relations assert clearly a *trend in time* by describing the direction of the energy transfer and postulating **irreversibility** of various thermodynamic processes.

The second law of thermodynamics is *not* a balance principle. It indicates a trend in both living and inanimate systems, where the situation $\Gamma < 0$ never occurs (it would mean that molecules organize themselves globally). Unlike the mass or the energy, in general, the entropy is *not* a conserved quantity, i.e. $\Gamma \geq 0$.

A thermodynamic process is called **reversible** if it is not accompanied by any entropy production, i.e. $\Gamma = 0$. For each cycle the material response returns to its initial state. A reversible process is a very useful idealized limit of a real process. The associated state of a reversible process is in equilibrium; thus, the equal signs hold in (4.131) and (4.132). Reversible processes belong to the realm of **equilibrium thermodynamics**, also known as **reversible thermodynamics** which is (classical) thermostatics.

A real process is **irreversible** and characterized by (4.131) and (4.132) in which the strict inequalities hold. This indicates that the rate of change of entropy \dot{S} is always greater than the rate of entropy input \tilde{Q} . Irreversible processes are always associated with dissipation of energy studied in the realm of **non-equilibrium thermodynamics**, also known as **irreversible thermodynamics**. For the concept of different thermodynamic theories the reader is referred to the review article by HUTTER [1977].

Clausius-Duhem inequality. The rate of entropy input is often closely related to the rate of thermal work (the total heat fluxes and sources). Very often the entropy fluxes \mathbf{h} , \mathbf{H} and the entropy sources \tilde{r} , \tilde{R} are assumed to be related to the heat fluxes \mathbf{q} , \mathbf{Q} and heat sources r , R by the proportional factor $1/\Theta$. Thereby $\Theta = \Theta(\mathbf{x}, t) > 0$ denotes a time-dependent scalar field known as the **absolute temperature**. The corresponding unit of temperature is called a **Kelvin**, denoted by K, which always has positive values.

However, in practice Θ is often measured in '*Celsius temperature*' or '*Fahrenheit temperature*' for which the unit is called the **degree Celsius** °C or the **degree Fahrenheit** °F, respectively. It is important to note that from the thermodynamic point of view the Celsius scale and the Fahrenheit scale are not true temperature scales at all. The temperatures on these scales can be negative, the zero is incorrect and temperature ratios are inconsistent with those required by the thermodynamic principles.

We postulate

$$\mathbf{h} = \frac{\mathbf{q}}{\Theta} , \quad \tilde{r} = \frac{r}{\Theta} \quad \text{and} \quad \mathbf{H} = \frac{\mathbf{Q}}{\Theta} , \quad \tilde{R} = \frac{R}{\Theta} , \quad (4.133)$$

but note, however, that these relations are, for example, inconsistent with the consequences of the kinetic theory of ideal gases and therefore not valid for the thermodynamics of diffusion.

With relations (4.133) and eqs. (4.129) and (4.130) we find from the second law of thermodynamics in the form of (4.132) that

$$\Gamma(t) = \frac{D}{Dt} \int_{\Omega} \eta_c dv + \int_{\partial\Omega} \frac{\mathbf{q}}{\Theta} \cdot \mathbf{n} ds - \int_{\Omega} \frac{r}{\Theta} dv \geq 0 , \quad (4.134)$$

$$\Gamma(t) = \frac{D}{Dt} \int_{\Omega_0} \eta dV + \int_{\partial\Omega_0} \frac{\mathbf{Q}}{\Theta} \cdot \mathbf{N} dS - \int_{\Omega_0} \frac{R}{\Theta} dV \geq 0 , \quad (4.135)$$

which is known as the **Clausius-Duhem inequality** here presented in the spatial and material descriptions, respectively. The Clausius-Duhem inequality is widely used in modern thermodynamic research initiated by TRUESDELL and TOUPIN [1960] and first clearly studied in the work of COLEMAN and NOLL [1963].

In order to derive the local form, which we only present in the material description, we convert the surface integral in eq. (4.135) to a volume integral according to the divergence theorem (1.297). By the product rule (1.287) we obtain

$$\int_{\partial\Omega_0} \frac{\mathbf{Q}}{\Theta} \cdot \mathbf{N} dS = \int_{\Omega_0} \operatorname{Div} \left(\frac{\mathbf{Q}}{\Theta} \right) dV = \int_{\Omega_0} \left(\frac{1}{\Theta} \operatorname{Div} \mathbf{Q} - \frac{1}{\Theta^2} \mathbf{Q} \cdot \operatorname{Grad} \Theta \right) dV , \quad (4.136)$$

where $\operatorname{Grad} \Theta$ denotes the material gradient of the smooth temperature field Θ .

By substituting eq. (4.136)₂ back into (4.135) and noting that the reference volume V is arbitrary and independent of time, the local form of the Clausius-Duhem inequality in the material description reads, in symbolic and index notation,

$$\begin{aligned} \dot{\eta} - \frac{R}{\Theta} + \frac{1}{\Theta} \operatorname{Div} \mathbf{Q} - \frac{1}{\Theta^2} \mathbf{Q} \cdot \operatorname{Grad} \Theta &\geq 0 , \\ \text{or} \quad \dot{\eta} - \frac{R}{\Theta} + \frac{1}{\Theta} \frac{\partial Q_A}{\partial X_A} - \frac{1}{\Theta^2} Q_A \frac{\partial \Theta}{\partial X_A} &\geq 0 . \end{aligned} \quad (4.137)$$

An alternative local version results, for example, from (4.137) by elimination of the heat source R by means of eq. (4.128), leading to

$$\begin{aligned} \mathbf{P} : \dot{\mathbf{F}} - \dot{e} + \Theta \dot{\eta} - \frac{1}{\Theta} \mathbf{Q} \cdot \operatorname{Grad} \Theta &\geq 0 , \\ \text{or} \quad P_{aA} \dot{F}_{aA} - \dot{e} + \Theta \dot{\eta} - \frac{1}{\Theta} Q_A \frac{\partial \Theta}{\partial X_A} &\geq 0 . \end{aligned} \quad (4.138)$$

The last term in eq. (4.138) determines **entropy production by conduction of heat**.

Clausius-Planck inequality and heat conduction. Based on physical observations heat flows from the warmer to the colder region of a body (free from sources of heat), not vice versa. Hence, entropy production by conduction of heat must be *non-negative*, i.e. $-(1/\Theta)\mathbf{Q} \cdot \operatorname{Grad} \Theta \geq 0$ (see the last term in (4.138)). The spatial version of this condition reads $-(1/\Theta)\mathbf{q} \cdot \operatorname{grad} \Theta \geq 0$, where $\operatorname{grad} \Theta$ denotes the spatial gradient of the smooth temperature field Θ .

Knowing that Θ is non-negative, we have

$$\mathbf{q} \cdot \operatorname{grad} \Theta \leq 0 \quad \text{or} \quad q_a \frac{\partial \Theta}{\partial x_a} \leq 0 , \quad (4.139)$$

$$\mathbf{Q} \cdot \operatorname{Grad} \Theta \leq 0 \quad \text{or} \quad Q_A \frac{\partial \Theta}{\partial X_A} \leq 0 , \quad (4.140)$$

which is known as the classical **heat conduction inequality**, here presented in terms of spatial and material coordinates, respectively. The heat conduction inequality expresses that heat does flow against a temperature gradient. It imposes an essential restriction on the heat flux vector.

Obviously the Cauchy heat flux \mathbf{q} depends on the spatial temperature gradient. With restriction (4.139) we may deduce that $\mathbf{q}(\text{grad}\Theta) \cdot \text{grad}\Theta \leq 0$ holds identically if $\text{grad}\Theta = \mathbf{0}$. Therefore, the dot product takes on a local maximum at $\text{grad}\Theta = \mathbf{0}$ and its derivative must vanish. Consequently, $\mathbf{q} = \mathbf{0}$ is implied, which means that there is no heat flux without a temperature gradient.

According to restriction (4.140), the Clausius-Duhem inequality (4.138) leads to an alternative *stronger form* of the second law of thermodynamics, often referred to as the **Clausius-Planck inequality**, i.e.

$$\mathcal{D}_{\text{int}} = \mathbf{P} : \dot{\mathbf{F}} - \dot{e} + \Theta \dot{\eta} \geq 0 \quad \text{or} \quad \mathcal{D}_{\text{int}} = P_{aA} \dot{F}_{aA} - \dot{e} + \Theta \dot{\eta} \geq 0 , \quad (4.141)$$

with the **internal dissipation or local production of entropy** $\mathcal{D}_{\text{int}} \geq 0$, which is required to be non-negative at any particle of a body for all times.

The non-negative internal dissipation \mathcal{D}_{int} consists of three terms: the work conjugate pair $\mathbf{P} : \dot{\mathbf{F}}$, i.e. the rate of internal mechanical work (or stress-power) per unit reference volume, then the rate of internal energy, \dot{e} , and the absolute temperature multiplied by the rate of entropy, $\Theta \dot{\eta}$. The internal dissipation is zero for reversible processes while the inequality holds for irreversible processes.

By means of the Clausius-Planck inequality (4.141), the local form of the balance of energy (4.128) can be rephrased in the convenient **entropy form**

$$\Theta \dot{\eta} = -\text{Div} \mathbf{Q} + \mathcal{D}_{\text{int}} + R \quad \text{or} \quad \Theta \dot{\eta} = -\frac{\partial Q_A}{\partial X_A} + \mathcal{D}_{\text{int}} + R , \quad (4.142)$$

in which the local evolution (change) of the entropy η appears explicitly.

A suitable constitutive assertion which relates the Cauchy heat flux $\mathbf{q} = \mathbf{q}(\mathbf{x}, t)$ in $\mathbf{x} = \chi(\mathbf{X}, t)$ to the spatial temperature gradient $\text{grad}\Theta = \text{grad}\Theta(\mathbf{x}, t)$ is furnished by

$$\mathbf{q} = -\kappa \text{grad}\Theta \quad \text{or} \quad q_a = -\kappa_{ab} \frac{\partial \Theta}{\partial x_b} . \quad (4.143)$$

This classical (phenomenological) law is motivated by experimental observations and is known as **Duhamel's law of heat conduction**, here presented in the spatial description.

The symmetric second-order tensor κ denotes the **spatial thermal conductivity tensor**; its components $\kappa_{ab} = \kappa_{ba}$ are either constants or functions of deformation and temperature. Substituting Duhamel's law of heat conduction (4.143) into restriction (4.139) we obtain $\kappa \text{grad}\Theta \cdot \text{grad}\Theta \geq 0$. This implies that κ is a positive semi-definite tensor at each \mathbf{x} .

EXAMPLE 4.6 Derive Duhamel's law of heat conduction in terms of material coordinates,

$$\mathbf{Q} = -\mathbf{F}^{-1}\kappa_0\mathbf{F}^{-T}\text{Grad}\Theta \quad \text{or} \quad Q_A = -F_{AB}^{-1}\kappa_{0BC}F_{DC}^{-1}\frac{\partial\Theta}{\partial X_D} , \quad (4.144)$$

where \mathbf{F}^{-1} is the inverse of the deformation gradient \mathbf{F} according to eq. (2.40) and $\kappa_0 = J\kappa$ denotes the positive semi-definite **material thermal conductivity tensor**. The volume ratio is $J = \det\mathbf{F} > 0$.

Solution. In order to show eq. (4.144) we need an expression between the spatial and the material temperature gradients. By using the absolute temperature Θ instead of Φ in relation (2.47) we find that

$$\text{grad}\Theta = \mathbf{F}^{-T}\text{Grad}\Theta . \quad (4.145)$$

Subsequently, by recalling the Piola transformation (4.121) for the heat flux vector we obtain from eq. (4.143)

$$J^{-1}\mathbf{F}\mathbf{Q} = -\kappa\mathbf{F}^{-T}\text{Grad}\Theta , \quad (4.146)$$

which after recasting gives the desired result (4.144). Since κ_0 is a positive semi-definite tensor the imposed restriction on the inequality (4.140) is satisfied. ■

If κ is an isotropic tensor we say that the material is **thermally isotropic** (no preferred direction for the heat conduction). For such a type of material the conductivity tensors become $\kappa = k\mathbf{I}$ and $\kappa_0 = k_0\mathbf{I}$. These relations substituted into (4.143) and (4.144) give

$$\mathbf{q} = -k\text{grad}\Theta \quad \text{or} \quad q_a = -k\frac{\partial\Theta}{\partial x_a} , \quad (4.147)$$

$$\mathbf{Q} = -k_0\mathbf{C}^{-1}\text{Grad}\Theta \quad \text{or} \quad Q_A = -k_0C_{AB}^{-1}\frac{\partial\Theta}{\partial X_B} , \quad (4.148)$$

where $\mathbf{C}^{-1} = \mathbf{F}^{-1}\mathbf{F}^{-T}$ characterizes the inverse of the right Cauchy-Green tensor \mathbf{C} .

The scalars $k \geq 0$ and $k_0 = Jk \geq 0$ denote **coefficients of thermal conductivity** (constants or, in general, deformation and temperature-dependent) and are naturally associated with the current and reference configurations of a body, respectively. The conditions $k \geq 0$ and $k_0 \geq 0$ imply that heat is conducted in the direction of decreasing temperature.

The relations (4.147) and (4.148) are well-known as **Fourier's law of heat conduction** which are basically constitutive relations.

Types of thermodynamic processes. Finally, we formulate special cases of thermodynamic processes and introduce some common terminology.

If the heat flux $q_n = -\mathbf{q} \cdot \mathbf{n}$ across the surface $\partial\Omega$ of a certain region Ω ($Q_N = -\mathbf{Q} \cdot \mathbf{N}$ on $\partial\Omega_0$), and the heat source r in that region Ω (R in Ω_0) vanish for all points of a body at each time, then a thermodynamic process is said to be **adiabatic** (coming from the Greek word *αδιάβατος*, which means impassable). This definition is based on the work of TRUESDELL and TOUPIN [1960, Section 258]. However, in engineering thermodynamics an adiabatic process is frequently defined as a process which cannot involve any heat transfer, $q_n = 0$ (or $Q_N = 0$). This means that the heat source r (or R) need not be zero.

In our case an adiabatic process is based on the condition that thermal energy can neither cross (enter or leave) the boundary surface nor be generated or destroyed within the body, so that the thermal power Q is zero (compare with eq. (4.118)). Additionally, under the assumption of relations (4.133) the rate of entropy input \tilde{Q} is also zero (compare with eq. (4.130)). Consequently, the second law of thermodynamics in the form of (4.131) reads $\Gamma = \dot{S} \geq 0$, which means that the total entropy S cannot decrease in an adiabatic process. Nevertheless, the entropy η at all points and times is not necessarily non-decreasing.

For an adiabatic process the energy balance equation, for example, in the entropy form (4.142), degenerates to

$$\Theta\dot{\eta} = \mathcal{D}_{\text{int}} . \quad (4.149)$$

If, in addition, an adiabatic process is *reversible* (no entropy is produced ($\Gamma = 0$), entailing that \dot{S} is zero), the balance equation (4.149) reduces further to

$$\Theta\dot{\eta} = \mathcal{D}_{\text{int}} = 0 , \quad (4.150)$$

which has some important applications in thermodynamics.

If the absolute temperature Θ during a thermodynamic process remains constant ($\dot{\Theta} = 0$), the process is said to be **isothermal** and if the entropy S possessed by a body remains constant ($\dot{S} = 0$), the process is said to be **isentropic**.

For an isentropic process the second law of thermodynamics (4.131) takes on the form $\Gamma = -\tilde{Q} \geq 0$. Hence, the local form of the Clausius-Duhem inequality in the material description (4.137) in symbolic and index notation degenerates to

$$\begin{aligned} & -R + \text{Div}\mathbf{Q} - \frac{1}{\Theta}\mathbf{Q} \cdot \text{Grad}\Theta \geq 0 , \\ \text{or} \quad & -R + \frac{\partial Q_A}{\partial X_A} - \frac{1}{\Theta}Q_A \frac{\partial \Theta}{\partial X_A} \geq 0 . \end{aligned} \quad (4.151)$$

If an isentropic process is *reversible*, the rate of entropy input \tilde{Q} (and the thermal power Q via assumption (4.133)) is zero since there is no entropy production Γ anymore. For this special case the equal signs in (4.151) hold. Consequently, it is im-

portant to note that *adiabatic processes* and *isentropic processes* are identical for the case in which both are *reversible*.

In discussing deformations of elastic materials (see Chapter 6) it is convenient to work with the strain-energy function Ψ introduced in eq. (4.116)₂. However, for the case in which Ψ is used within the thermodynamic regime incorporating thermal variables such as Θ or η , then Ψ is commonly referred to as the **Helmholtz free-energy function** or referred to briefly as the **free energy**.

Next, we express the Helmholtz free-energy function in terms of the internal energy e and the entropy η . Having in mind this aim, we apply the **Legendre transformation**, generally defining a procedure which replaces one or some variables with the conjugate variables, particularly used in analytical mechanics (see, for example, ABRAHAM and MARSDEN [1978]). We may write

$$\Psi = e - \Theta\eta . \quad (4.152)$$

Note that all three quantities Ψ, e, η are introduced so that they refer to a unit volume of the reference configuration.

By using the material time derivative of the free energy, i.e. $\dot{\Psi} = D\Psi/Dt$, we may write the Clausius-Planck inequality (4.141) in the convenient form

$$\mathcal{D}_{int} = \mathbf{P} : \dot{\mathbf{F}} - \dot{\Psi} - \eta\dot{\Theta} \geq 0 , \quad (4.153)$$

often employed when the absolute temperature is used as an independent variable.

Note that for the case of a purely mechanical theory, that is, if thermal effects are ignored (Θ and η are omitted), inequality (4.153) degenerates to

$$\mathcal{D}_{int} = w_{int} - \dot{\Psi} \geq 0 , \quad (4.154)$$

and the free energy Ψ coincides with the internal energy e (see the Legendre transformation (4.152)). For a reversible process for which the internal dissipation \mathcal{D}_{int} is zero (no entropy production, $\Gamma = 0$), we conclude from (4.154) that the rate of internal mechanical work (or stress-power) $w_{int} = \mathbf{P} : \dot{\mathbf{F}}$ per unit reference volume (see eq. (4.113)) equals $\dot{\Psi}$.

EXERCISES

1. Recall relation (4.145) and Piola transformation (4.121) for the heat flux vector. Show the equivalence of relations (4.139) and (4.140) with manipulations according to identity (1.81).
2. Starting from (4.132), show that the local spatial form of the second law of thermodynamics is

$$\frac{\partial \eta_c}{\partial t} \geq -\text{div}(\mathbf{h} + \eta_c \mathbf{v}) + \bar{r}$$

(compare with Exercise 2 on p. 166).

3. Derive the local forms of the Clausius-Duhem inequality and the Clausius-Planck inequality in the spatial description associated with (4.137), (4.138) and (4.141), (4.142), respectively. Note the fact that the internal energy and the entropy possessed by a body were introduced per unit *volume* rather than per unit *mass* (see relations (4.91) and (4.129)).

Hint: Use Reynold's transport theorem in the form of (4.26).

4. Show that if the absolute temperature Θ is merely a function of time, the Clausius-Duhem inequality and the Clausius-Planck inequality coincide, leading to the local material form

$$\Theta \dot{\eta} \geq R - \text{Div} \mathbf{Q} \quad \text{or} \quad \Theta \dot{\eta} \geq R - \frac{\partial Q_A}{\partial X_A} ,$$

also valid for isothermal processes.

4.7 Master Balance Principle

We recognize from previous sections that conservation of mass, the momentum balance principles and the two fundamental laws of thermodynamics are all of the same mathematical structure. To generalize these relations is the objective of the following section.

Master balance principle in the global form. The present status of a set of particles occupying an arbitrary region Ω of a continuum body \mathcal{B} with boundary surface $\partial\Omega$ at time t may be characterized by a tensor-valued function $I(t) = \int_{\Omega} f dv$ (compare with eq. (4.22)). In the following let $f = f(\mathbf{x}, t)$ be a smooth spatial tensor field per unit current volume of order n . In particular, f may characterize some physical scalar, vector or tensor quantity such as *density*, *linear* and *angular momentum*, *total energy* and so forth.

A change of these quantities may now be expressed as the following **master balance principle** here presented in the global spatial form

$$\frac{D}{Dt} \int_{\Omega} f(\mathbf{x}, t) dv = \int_{\partial\Omega} \phi(\mathbf{x}, t, \mathbf{n}) ds + \int_{\Omega} \Sigma(\mathbf{x}, t) dv . \quad (4.155)$$

The first term on the right-hand side is the integral of the so-called **surface density** $\phi = \phi(\mathbf{x}, t, \mathbf{n})$, which is a tensor of order n . The surface density is defined per unit current area and distributed over the boundary surface $\partial\Omega$. Note that ϕ depends not only on position \mathbf{x} and time t , but also on the orientation of the infinitesimal spatial