

Mass- and volume-specific views on thermodynamics for open systems

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A general framework for the thermodynamics of open systems is presented. The theory is fundamentally based on the generalized balance of mass, which is enhanced by additional surface-flux and volume-source terms. The presentation highlights the influence of the enhanced mass balance on the remaining balance equations. To clarify the impact of the variable reference density, we introduce the notions of volume-specific and mass-specific formats. Particular attention is drawn to the fact that the mass-specific balance equations are free from explicit open-system contributions. They resemble the classical balance equations and can thus be evaluated in complete analogy to the closed-system case. Restrictions for the constitutive equations follow from the second law of thermodynamics, as illustrated for the particular model problem of thermo-hyperelasticity.

Keywords: thermodynamics; open systems; changes in density; biomechanics; chemomechanics

1. Introduction

In classical thermodynamics, the amount of matter within a fixed material domain is typically assumed to be constant throughout the entire thermodynamical process. Conceptually speaking, classical thermodynamics deals with ‘closed systems’ for which the exchange of material with the environment is *a priori* excluded. For most traditional applications, the conservation of mass, which is nothing but a mere definition, yields appropriate results. Nevertheless, within the last few decades, the field of application of thermodynamics, supplemented by appropriate computational-solution techniques, has been growing tremendously. Biomechanical and chemomechanical problems furnish typical examples of recent fields of interest. As opposed to the traditional applications, both biomechanics and chemomechanics typically fall within the category of ‘open-system’ mechanics allowing for the influx or the local creation of mass. Consequently, the traditional balance of mass has to be enhanced by additional open-system contributions. However, the exchange of matter with the environment affects not only the balance of mass since the newly generated or inflowing mass typically carries a specific amount of momentum, energy and entropy. Thus, all the other balance equations also have to be reconsidered in the view of open-system thermodynamics.

The ‘theory of open systems’ is closely related to the ‘theory of mixtures’, as proposed by Truesdell & Toupin (1960), Bowen (1976) and Runesson (1978) or

more recently by Wu *et al.* (1998), de Boer (2000), Diebels (2000), Ehlers (2002) or Humphrey & Rajagopal (2002). Every individual component of the mixture can be interpreted locally as an open system undergoing a thermomechanical exchange with the ‘outside world’, represented by the remaining constituents of the mixture (see, for example, Haupt 2000). The loss or gain of mass of one constituent is thus compensated by the others, while the overall mass of the mixture itself remains constant. The ‘theory of mixtures’ is based on the fundamental assumption that the individual constituents are superposed locally at each point in space. However, if the individual components are spatially separated and the overall behaviour is primarily determined by one constituent alone, it seems reasonable to confine attention to only a part of the overall matter present by making use of the ‘theory of open systems’.

Following the line of thought introduced by Maugin (1999, § 2.1), an open system can be understood as being enclosed by a permeable, deformable and diathermal membrane, through which an exchange of mass, momentum, energy and entropy can take place. In the context of biomechanics, the first model allowing for this type of exchange in terms of volume contributions was introduced by Cowin & Hegedus (1976) under the name of the ‘theory of adaptive elasticity’. A natural extension to the additional surface flux terms has been presented recently by Epstein & Maugin (2000) as the ‘theory of volumetric growth’. Proliferation, hyperplasia, hypertrophy and atrophy can be identified as typical sources of mass, while the migration or movement of cells is a classical example of a mass flux in biomechanical applications (see, for example, Taber 1995; Humphrey 2002).

A classical example in chemomechanics, which can be found in nearly every textbook of mechanics, is furnished by the motion of a burning body typically encountered in rocket propulsion (see, for example, Truesdell & Toupin 1960, § 155; Goldstein 1950, § 1.6; Müller 1994, § 1.4.6; Haupt 2000, § 3.5). The open system of the rocket, consisting of the rocket hull plus the amount of fuel, experiences a permanent loss of mass due to combustion and ejection. Thus, the balance of mass of the rocket states that the time rate of change of the overall rocket mass m be in equilibrium with the rate of mass ejection \mathfrak{R} ,

$$D_t m = \mathfrak{R},$$

whereby $\mathfrak{R} \leq 0$. The ‘volume-specific’ version of the balance of momentum balances the time rate of change of the overall momentum $\mathbf{p} = m\mathbf{v}$, the velocity \mathbf{v} weighted by the actual mass m , with the total force \mathbf{f} acting on it.

$$D_t \mathbf{p} = \mathbf{f} \quad \text{with} \quad \mathbf{f} = \mathbf{f}^{\text{closed}} + \mathbf{f}^{\text{open}} \quad \text{and} \quad \mathbf{f}^{\text{open}} = \bar{\mathbf{f}}^{\text{open}} + \mathbf{v}\mathfrak{R}.$$

Herein, $\mathbf{f}^{\text{closed}}$ denotes the standard mechanical forces. The third term, $\mathbf{v}\mathfrak{R}$, explicitly accounts for the amount of momentum generated by the ejected mass leaving the system at the same velocity as the rocket itself, while the second term \mathbf{f}^{open} accounts for the difference in the velocity of the ejection $\bar{\mathbf{v}}$ with respect to the rocket-head velocity \mathbf{v} , thus $\mathbf{f}^{\text{open}} = [\bar{\mathbf{v}} - \mathbf{v}]\mathfrak{R}$. With the help of the definition of the overall rocket momentum as $\mathbf{p} = m\mathbf{v}$, the ‘mass-specific’ version of the balance of momentum can be constructed by subtracting \mathbf{v} times the balance of mass from the volume-specific version:

$$mD_t \mathbf{v} = \bar{\mathbf{f}} \quad \text{with} \quad \bar{\mathbf{f}} = \mathbf{f}^{\text{closed}} + \bar{\mathbf{f}}^{\text{open}} \quad \text{and} \quad \bar{\mathbf{f}}^{\text{open}} = [\bar{\mathbf{v}} - \mathbf{v}]\mathfrak{R}.$$

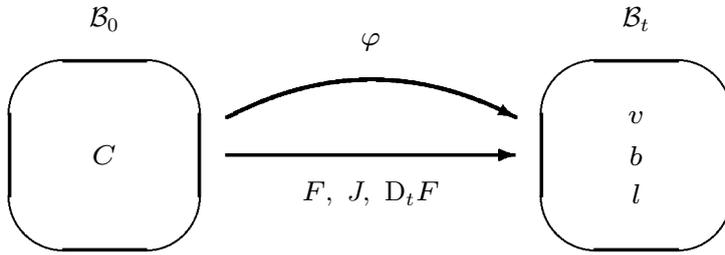


Figure 1. Kinematics.

The force $\bar{\mathbf{f}}^{\text{open}}$ responsible for changes in the rocket velocity \mathbf{v} is typically called ‘propulsive force’ or ‘rocket thrust’.

This contribution aims at providing a general framework for open-system thermodynamics. Our primary goal is to derive the appropriate field equations in the form of the balance of mass, momentum, energy and entropy to determine the fields of the density, motion and temperature as a function of time. To keep the underlying theory as general as possible, mass exchanges are allowed to take place through the in- or outflux of matter via the domain boundary and through the creation of mass within the domain itself. The impact of these mass exchanges on the remaining balance equations is explored by distinguishing strictly between the ‘volume-specific’ and the ‘mass-specific’ format as illustrated in the model problem of rocket propulsion. As indicated in the example, the local changes in mass manifest themselves in two contributions, one assuming that the newly generated mass carries the same amount of mass-specific momentum, energy and entropy as the original substrate, the other accounting for a possible difference in these quantities. While the volume-specific format contains both types of terms, the mass-specific balance equations are free from all the explicit mass-dependent terms and only account for the latter contribution. Consequently, the mass-specific balance equations take the familiar structure typically encountered in classical thermodynamics.

This paper is organized as follows. Section 2 defines the basic notation and reiterates the relevant kinematic relations. The balance of mass, the fundamental equation of open-system thermodynamics, is introduced in § 3. Section 4 illustrates the influence of the enhanced mass balance on the balance of momentum which is discussed in the volume-specific and in the mass-specific formats. The balance of angular momentum and the balance of kinetic energy follow as natural byproducts. In § 5, the balance of total and internal energy are derived. Section 6 is dedicated to the balance of entropy, which finally lends itself to the Clausius–Duhem inequality, placing further restrictions to the constitutive assumptions. The evaluation of the Clausius–Duhem inequality is illustrated in § 7 for the model problem of thermo-hyperelasticity.

2. Kinematics

The kinematic description is based on the spatial-motion map,

$$x = \varphi(X, t) : \mathcal{B}_0 \rightarrow \mathcal{B}_t, \tag{2.1}$$

mapping the material placement X of a physical particle in the material configuration \mathcal{B}_0 to its spatial placement x in the spatial configuration \mathcal{B}_t (see figure 1). The related

spatial-deformation gradient F and its Jacobian J ,

$$F = \nabla_X \varphi(X, t) : T\mathcal{B}_0 \rightarrow T\mathcal{B}_t, \quad J = \det F > 0, \tag{2.2}$$

define the linear tangent map from the material tangent space $T\mathcal{B}_0$ to the spatial tangent space $T\mathcal{B}_t$. Typically, the right and left Cauchy–Green strain tensors C and b ,

$$C = F^t \cdot F, \quad b = F \cdot F^t, \tag{2.3}$$

or their inverses, $B = C^{-1}$ and $c = b^{-1}$, are introduced as characteristic strain measures. Moreover, we shall distinguish between the material time derivative $D_t = \partial_t \{\bullet\}|_X$ of mass-specific quantity $\{\bullet\}$ at fixed material placement X and the spatial time derivative $d_t = \partial_t \{\bullet\}|_x$ at fixed spatial placement x . The material and the spatial time derivative of any scalar- or vector-valued mass-specific quantity $\{\bullet\}$ are related via the Euler theorem,

$$D_t \{\bullet\} = d_t \{\bullet\} + \nabla_x \{\bullet\} \cdot v, \tag{2.4}$$

through the convective term $\nabla_x \{\bullet\} \cdot v$. The spatial velocity v is introduced as the material time derivative of the spatial-motion map φ :

$$v = D_t \varphi(X, t). \tag{2.5}$$

Its material gradient $\nabla_X v$ is identical to the material time derivative of the spatial-deformation gradient F , while the spatial-velocity gradient $\nabla_x v$ will be denoted as l in the following equation:

$$D_t F = \nabla_X v, \quad l = \nabla_x v. \tag{2.6}$$

With these definitions at hand, the material time derivative of the Jacobian J can be expressed through the well-known Euler identity $D_t J = J \operatorname{div} v$ with $\operatorname{div} v = F^{-t} : D_t F$ denoting the spatial divergence of the spatial velocity v . In the following, we will distinguish between volume-specific scalar-valued or tensorial quantities with material reference $\{\bullet\}_0 = \rho_0 \{\bullet\}$ and with spatial reference $\{\bullet\}_t = \rho_t \{\bullet\}$, whereby $\{\bullet\}$ denotes the mass-specific density. The integration of a quantity with material reference over the material domain \mathcal{B}_0 yields the identical result as the integration of a quantity with spatial reference over the spatial domain \mathcal{B}_t :

$$\int_{\mathcal{B}_0} \{\bullet\}_0 \, dV = \int_{\mathcal{B}_t} \{\bullet\}_t \, dv. \tag{2.7}$$

The local counterpart of the above equation defines the classical relation between volume-specific material and spatial quantities:

$$\{\bullet\}_0 = J \{\bullet\}_t. \tag{2.8}$$

Correspondingly, we can relate any vector- or tensor-valued surface flux $\{\square\}$ through the boundary of the material domain $\partial\mathcal{B}_0$ to the corresponding contribution $\{\diamond\}$ through the spatial boundary $\partial\mathcal{B}_t$,

$$\int_{\partial\mathcal{B}_0} \{\square\} \cdot dA = \int_{\partial\mathcal{B}_t} \{\diamond\} \cdot da. \tag{2.9}$$

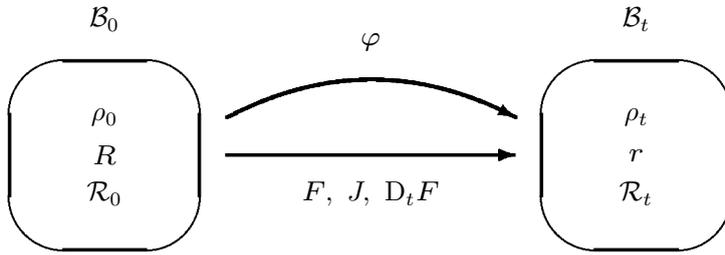


Figure 2. Balance of mass: densities, fluxes and sources.

By making use of the classical Nanson formula from 1878 as $da = JF^{-t} \cdot dA$ we obtain the local counterpart of the above equation,

$$\{\square\} = J\{\diamond\} \cdot F^{-t}, \tag{2.10}$$

a relation between the material and the spatial surface fluxes, which can alternatively be expressed as $\text{Div}\{\square\} = J \text{div}\{\diamond\}$. Moreover, we will make use of the differential form of Reynolds’s transport theorem,

$$jD_t\{\bullet\}_0 = d_t\{\bullet\}_t + \text{div}(\{\bullet\}_t \otimes v), \tag{2.11}$$

which follows from the above considerations. It states that the material time rate of change of the volume-specific quantity $\{\bullet\}_0$ in a material domain \mathcal{B}_0 is equal to the spatial time rate of change of the volume-specific quantity $\{\bullet\}_t$ in the spatial domain \mathcal{B}_t plus the flux $\{\bullet\}_t \otimes v$ through the surface $\partial\mathcal{B}_t$ of the moving domain. While Reynolds’s transport theorem (2.11) will later on be applied to relate spatial and material quantities in the volume-specific format, the Euler theorem (2.4) will serve to relate the corresponding mass-specific quantities.

With the introduced definitions at hand, we will now elaborate the balance equations for open systems. For the sake of transparency, we shall assume that sufficient smoothness criteria are fulfilled by the related fields of the balanced quantity itself $\{\bullet\}_0$ or $\{\bullet\}_t$, the related fluxes $\{\square\}$ and $\{\diamond\}$ and the corresponding source terms $\{\circ\}_0$ and $\{\circ\}_t$. Consequently, instead of analysing the global or integral form of the balance laws,

$$\left. \begin{aligned} D_t \int_{\mathcal{B}_0} \{\bullet\}_0 dV &= \int_{\partial\mathcal{B}_0} \{\square\} \cdot dA + \int_{\mathcal{B}_0} \{\circ\}_0 dV, \\ d_t \int_{\mathcal{B}_t} \{\bullet\}_t dv + \int_{\partial\mathcal{B}_t} [\{\bullet\}_t \otimes v] \cdot da &= \int_{\partial\mathcal{B}_t} \{\diamond\} \cdot da + \int_{\mathcal{B}_t} \{\circ\}_t dv, \end{aligned} \right\} \tag{2.12}$$

we will restrict ourselves to their local or rather differential format:

$$\left. \begin{aligned} D_t\{\bullet\}_0 &= \text{Div}\{\square\} + \{\circ\}_0, \\ d_t\{\bullet\}_t + \text{div}(\{\bullet\}_t \otimes v) &= \text{div}\{\diamond\} + \{\circ\}_t. \end{aligned} \right\} \tag{2.13}$$

3. Balance of mass

In classical non-relativistic mechanics of closed systems, the quantity of matter in a body \mathcal{B}_0 does not change, irrespective of the motion, the deformation and the acceleration of the body. However, this conservation of mass is a mere definition which is

no longer valid for open systems like the ones considered here. In abstract terms, the local balance of mass of open systems states that the rate of change of the material or spatial density ρ_0 or ρ_t is equal to the sum of the divergence of the related mass flux R or r and the mass source \mathcal{R}_0 or \mathcal{R}_t (see figure 2). Note that most existing theories for open systems, except for the one developed by Epstein & Maugin (2000), *a priori* exclude the in- or outflux of mass as $R = \mathbf{0}$ and $r = \mathbf{0}$. The leaching of portlandite or the progressive decalcification of the calcium silicate hydrates in concrete furnish typical examples of an outflux of mass in chemomechanical applications. Cell migration is another example of a mass flux typically encountered in biomechanical problems. In principle, it always is possible to express any flux term R or r through an equivalent source term of the form $\text{Div } R$ or $\text{div } r$ according to the ‘equivalence of surface and volume sources’ as stated by Truesdell & Toupin (1960, § 157). However, we shall allow for independent flux terms in the following to keep the underlying theory as general as possible. Consequently, the material version of the balance of mass can be stated as

$$D_t \rho_0 = \text{Div } R + \mathcal{R}_0. \tag{3.1}$$

The individual terms in the above equation can be pushed forward with the help of the standard Piola transforms

$$\rho_0 = J \rho_t, \quad \mathcal{R}_0 = J \mathcal{R}_t, \quad R = J r \cdot F^{-t}. \tag{3.2}$$

Note that in classical continuum mechanics with $R = \mathbf{0}$ and $\mathcal{R}_0 = 0$, equation (3.2)₁ is usually referred to as the ‘material continuity equation’. The application of Reynolds’s transport theorem (2.11),

$$j D_t \rho_0 = d_t \rho_t + \text{div}(\rho_t v), \tag{3.3}$$

introduces the spatial version of the balance of mass,

$$d_t \rho_t + \text{div}(\rho_t v) = \text{div } r + \mathcal{R}_t. \tag{3.4}$$

Equation (3.4), which was introduced as the ‘spatial continuity equation’ by Euler in 1757, represents one of the basic equations in classical fluid mechanics in the context of closed systems with $r = \mathbf{0}$ and $\mathcal{R}_t = 0$. In the following, we shall distinguish between the material and the spatial version of the balance of mass given in the form

$$D_t \rho_0 = \text{Div } R + \mathcal{R}_0, \quad d_t \rho_t + \text{div}(\rho_t v) = \text{div } r + \mathcal{R}_t. \tag{3.5}$$

Remark 3.1 (volume- and mass-specific formats). In the present theory, the balance of mass plays a central role, since it can essentially be used to transform the volume-specific version of any other balance law to its mass-specific counterpart. In the volume-specific format, the quantity to be balanced can either be given with material or spatial reference as $\{\bullet\}_0 = \rho_0 \{\bullet\}$ or $\{\bullet\}_t = \rho_t \{\bullet\}$. It is balanced with the sum of the divergence of the corresponding fluxes $\{\square\}$ and $\{\diamond\}$ and the volume sources $\{\circ\}_0$ and $\{\circ\}_t$:

$$D_t \{\bullet\}_0 = \text{Div} \{\square\} + \{\circ\}_0, \quad d_t \{\bullet\}_t + \text{div}(\{\bullet\}_t \otimes v) = \text{div} \{\diamond\} + \{\circ\}_t. \tag{3.6}$$

The material and spatial versions of a balance law, (3.6)₁ and (3.6)₂, respectively, are related through the corresponding Piola transforms $\{\bullet\}_0 = J \{\bullet\}_t$, $\{\circ\}_0 = J \{\circ\}_t$ and $\{\square\} = J \{\diamond\} \cdot F^{-t}$ in combination with Reynolds’s transport theorem (2.11).

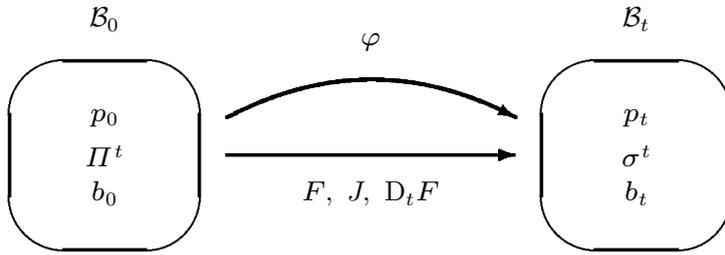


Figure 3. Balance of momentum: momentum densities, fluxes and sources.

Note that the fluxes $\{\square\}$ and $\{\diamond\}$ can be expressed in terms of the reduced flux terms $\{\bar{\square}\}$ and $\{\bar{\diamond}\}$ in the form

$$\{\square\} = \{\bar{\square}\} + \{\bullet\} \otimes R, \quad \{\diamond\} = \{\bar{\diamond}\} + \{\bullet\} \otimes r. \tag{3.7}$$

Correspondingly, the volume-specific source terms are defined in terms of the reduced source terms, $\{\bar{\circ}\}_0$ and $\{\bar{\circ}\}_t$:

$$\{\circ\}_0 = \{\bar{\circ}\}_0 + \{\bullet\}\mathcal{R}_0 - \nabla_X\{\bullet\} \cdot R, \quad \{\circ\}_t = \{\bar{\circ}\}_t + \{\bullet\}\mathcal{R}_t - \nabla_x\{\bullet\} \cdot r. \tag{3.8}$$

Each balance law can thus be transformed into a mass-specific version, balancing the rate of change of the mass-specific quantity $\{\bullet\} = \{\bullet\}_0/\rho_0$ or $\{\bullet\} = \{\bullet\}_t/\rho_t$ with the corresponding reduced flux $\{\bar{\square}\}$ and $\{\bar{\diamond}\}$ and the reduced source terms $\{\bar{\circ}\}_0$ and $\{\bar{\circ}\}_t$. The mass-specific balance equations can be derived by subtracting $\{\bullet\}$ times the balance of mass (3.5) from the corresponding volume-specific version, (3.6). Consequently, we obtain remarkably simple generic forms of the mass-specific balance laws,

$$\rho_0 D_t\{\bullet\} = \text{Div}\{\bar{\square}\} + \{\bar{\circ}\}_0, \quad \rho_t d_t\{\bullet\} + \rho_t v \cdot \nabla_x\{\bullet\} = \text{div}\{\bar{\diamond}\} + \{\bar{\circ}\}_t, \tag{3.9}$$

which are related through the Piola transforms $\{\bullet\}_0 = J\{\bullet\}_t$, $\{\bar{\circ}\}_0 = J\{\bar{\circ}\}_t$ and $\{\bar{\square}\} = J\{\bar{\diamond}\} \cdot F^{-t}$ and the Euler theorem (2.4). Note that the mass-specific format is free from all the explicit extra terms caused by the changes in mass. However, this is not the case in the formulation developed by Epstein & Maugin (2000), where the gradient terms $\nabla_X\{\bullet\} \cdot R$ and $\nabla_x\{\bullet\} \cdot r$ are part of the mass-specific balance equation (3.9).

4. Balance of momentum

Bearing in mind the derivation of the generic balance laws of the preceding section, we now elaborate their specification to yield the balance of linear momentum. It will turn out that the balance of angular momentum and the balance of kinetic energy can be interpreted as particular weighted versions of the balance of linear momentum.

(a) Volume-specific version

The balance of momentum represents one of the ‘laws of classical mechanics’. For closed systems, it was first specified by Euler in 1776. It states that, in an inertial frame, the reaction of any body is equal to the load acting upon it. Therein the reaction is characterized through the volume-specific momentum density p_0 or p_t ,

canonically defined as a spatial covector given through the partial derivative of the volume-specific kinetic-energy density K_0 or K_t ,

$$K_0 = \frac{1}{2}\rho_0 v \cdot v, \quad K_t = \frac{1}{2}\rho_t v \cdot v, \tag{4.1}$$

with respect to the spatial velocity v .

$$p_0 = \partial_v K_0 = \rho_0 v, \quad p_t = \partial_v K_t = \rho_t v. \tag{4.2}$$

The load can essentially be divided into two types, namely the contact or surface forces represented by the momentum fluxes Π^t and σ^t and the at-a-distance forces, i.e. the momentum sources b_0 and b_t (see figure 3). Consequently, the material version of the volume-specific balance of momentum, sometimes also referred to as ‘Cauchy’s first law of motion’, can be expressed as

$$D_t p_0 = \text{Div } \Pi^t + b_0. \tag{4.3}$$

In honour of the work of Piola in 1833 and Kirchhoff in 1852, the momentum flux Π^t is typically referred to as the first Piola–Kirchhoff stress tensor in classical continuum mechanics. With the help of the well-known Piola transforms

$$p_0 = J p_t, \quad b_0 = J b_t, \quad \Pi^t = J \sigma^t \cdot F^{-t}, \tag{4.4}$$

the individual terms of equation (4.3) can be pushed forward to the spatial configuration. The corresponding momentum flux σ^t is commonly denoted as the Cauchy stress tensor in standard continuum mechanics, commemorating the early work of Cauchy in 1823. The application of Reynolds’s transport theorem (2.11),

$$j D_t p_0 = d_t p_t + \text{div}(p_t \otimes v), \tag{4.5}$$

yields the spatial version of the balance of momentum,

$$d_t p_t + \text{div}(p_t \otimes v) = \text{div } \sigma^t + b_t, \tag{4.6}$$

which is typically applied in classical fluid mechanics. The overall flux term, $\sigma^t - p_t \otimes v$, reflects the convective nature of the above equation through the transport of linear momentum $p_t \otimes v$. In summary, we distinguish between the material and the spatial version of the volume-specific balance of momentum:

$$D_t p_0 = \text{Div } \Pi^t + b_0, \quad d_t p_t + \text{div}(p_t \otimes v) = \text{div } \sigma^t + b_t. \tag{4.7}$$

On the Neumann boundary, characterized through the material and spatial normal N and n , the normal projections of the momentum fluxes of Piola–Kirchhoff and Cauchy type, Π^t and σ^t , are required to be in equilibrium with the corresponding closed- and open-system stress-vector contributions t_0^{closed} or t_t^{closed} and t_0^{open} or t_t^{open} , respectively:

$$\left. \begin{aligned} \Pi^t \cdot N &= t_0^{\text{closed}} + t_0^{\text{open}}, & t_0^{\text{open}} &= \bar{t}_0^{\text{open}} + [p \otimes R] \cdot N, \\ \sigma^t \cdot n &= t_t^{\text{closed}} + t_t^{\text{open}}, & t_t^{\text{open}} &= \bar{t}_t^{\text{open}} + [p \otimes r] \cdot n. \end{aligned} \right\} \tag{4.8}$$

Correspondingly, the momentum sources terms b_0 and b_t can be understood as the sum of the closed- and the open-system volume-force contributions b_0^{closed} or b_t^{closed} and b_0^{open} or b_t^{open} :

$$\left. \begin{aligned} b_0 &= b_0^{\text{closed}} + b_0^{\text{open}}, & b_0^{\text{open}} &= \bar{b}_0^{\text{open}} + p \mathcal{R}_0 - \nabla_X p \cdot R, \\ b_t &= b_t^{\text{closed}} + b_t^{\text{open}}, & b_t^{\text{open}} &= \bar{b}_t^{\text{open}} + p \mathcal{R}_t - \nabla_x p \cdot r. \end{aligned} \right\} \tag{4.9}$$

While the expressions in terms of R , r , \mathcal{R}_0 and \mathcal{R}_t take into account the part of the newly created or inflowing mass that carries the same amount of mass-specific momentum p as the original substrate, the additional terms \bar{t}_0^{open} , \bar{t}_t^{open} , \bar{b}_0^{open} and \bar{b}_t^{open} account for a possible difference in the momentum density.

Remark 4.1 (balance of angular momentum). The volume-specific angular-momentum density l_0 or l_t is defined through the vector product of the corresponding linear momentum density p_0 or p_t with a distance vector $a = \varphi - \varphi_0$ from a fixed point φ_0 in space:

$$l_0 = a \times p_0, \quad l_t = a \times p_t. \tag{4.10}$$

In the absence of distributed couples and internal rotational degrees of freedom, the volume-specific balance of angular momentum for open systems can be derived by taking the vector product of the volume-specific momentum balance (4.7) with the distance vector a :

$$a \times D_t p_0 = a \times \text{Div } \Pi^t + a \times b_0. \tag{4.11}$$

With the definition of the angular momentum (4.10), the above equation can be rewritten as

$$D_t l_0 = \text{Div}(a \times \Pi^t) + a \times b_0 - F \times \Pi^t. \tag{4.12}$$

Thereby, the vector product of the two second-order tensors $-F \times \Pi^t$ can be expressed in terms of the axial vector of the related second-order tensor, $[F \cdot \Pi]^{\text{axl}}$, as $-F \times \Pi^t = 2[F \cdot \Pi]^{\text{axl}}$. It proves convenient for later purposes to reformulate the above statement in terms of the reduced momentum flux, $\bar{\Pi}^t = \Pi^t - p \otimes R$, and the reduced momentum source $\bar{b}_0 = b_0 - p\mathcal{R}_0 + \nabla_X p \cdot R$,

$$D_t l_0 = \text{Div}(a \times [\bar{\Pi}^t + p \otimes R]) + a \times [\bar{b}_0 + p\mathcal{R}_0 - \nabla_X p \cdot R] - F \times [\bar{\Pi}^t + p \otimes R]. \tag{4.13}$$

Herein, the third term on the right-hand side,

$$-F \times [\bar{\Pi}^t + p \otimes R] = 2[F \cdot [\bar{\Pi} + R \otimes p]]^{\text{axl}},$$

represents the volume-specific production of the angular momentum l_0 . Anticipating later considerations, we would like to point out that, assuming the symmetry of the reduced momentum flux $F \cdot \bar{\Pi} = \bar{\Pi}^t \cdot F^t$, or equivalently $\bar{\sigma} = \bar{\sigma}^t$, the production of angular momentum reduces to $2[F \cdot [R \otimes p]]^{\text{axl}}$ or $2[r \otimes p]^{\text{axl}}$, respectively.

Remark 4.2 (balance of kinetic energy). Although the balance of kinetic energy does not constitute an independent balance law, it proves significant to take a closer look at it, since it will help to introduce work conjugate stress and strain measures. Moreover, the balance of kinetic energy will be used to identify the external and internal mechanical power which are essential for our further thermodynamical considerations. The starting point is the material time derivative of the volume-specific kinetic-energy density $K_0 = \frac{1}{2}\rho_0 v \cdot v$:

$$D_t K_0 = \rho_0 D_t K + K D_t \rho_0 = p_0 \cdot D_t v + K D_t \rho_0 = v \cdot D_t p_0 - K D_t \rho_0. \tag{4.14}$$

With the projection of the volume-specific balance of momentum (4.3) with the spatial velocity v and the balance of mass (3.5)₁ weighted by the mass-specific kinetic-energy density K ,

$$\left. \begin{aligned} v \cdot D_t p_0 &= \text{Div}(v \cdot \Pi^t) + v \cdot b_0 - \nabla_X v : \Pi^t, \\ K D_t \rho_0 &= \text{Div}(KR) + K\mathcal{R}_0 - \nabla_X K \cdot R, \end{aligned} \right\} \tag{4.15}$$

equation (4.14) can be rewritten in the explicit form

$$D_t K_0 = \text{Div}(v \cdot \Pi^t - KR) + v \cdot b_0 - K\mathcal{R}_0 + \nabla_X K \cdot R - \Pi^t : D_t F. \tag{4.16}$$

In what follows, it will prove convenient to reformulate the above equation in terms of the reduced momentum flux $\bar{\Pi}^t = \Pi^t - p \otimes R$ and the reduced momentum source $\bar{b}_0 = b_0 - p\mathcal{R}_0 + \nabla_X p \cdot R$ which can be related to their overall counterparts Π^t and b_0 through the following identities:

$$\left. \begin{aligned} \text{Div}(v \cdot \Pi^t) &= \text{Div}(v \cdot \bar{\Pi}^t) + \text{Div}(2KR), \\ v \cdot b_0 &= v \cdot \bar{b}_0 + 2K\mathcal{R}_0 - v \cdot \nabla_X p \cdot R, \\ \Pi^t : D_t F &= \bar{\Pi}^t : D_t F + p \cdot \nabla_X v \cdot R. \end{aligned} \right\} \tag{4.17}$$

With the help of the above equations and the identity $v \cdot \nabla_X p + p \cdot \nabla_X v = 2\nabla_X K$ following from $v \cdot p = 2K$, equation (4.16) can be reformulated in the following way:

$$D_t K_0 = \text{Div}(v \cdot \bar{\Pi}^t + KR) + v \cdot \bar{b}_0 + K\mathcal{R}_0 - \nabla_X K \cdot R - \bar{\Pi}^t : D_t F. \tag{4.18}$$

As stated by Stokes in 1857, the rate of change of the kinetic energy is equal to the external mechanical power minus the internal mechanical power. Consequently, the right-hand side of the above equation enables the identification of the volume-specific external and internal mechanical power ρ_0^{ext} and ρ_0^{int} ,

$$\left. \begin{aligned} \rho_0^{\text{ext}} &:= \text{Div}(v \cdot \bar{\Pi}^t + KR) + v \cdot \bar{b}_0 + K\mathcal{R}_0 - \nabla_X K \cdot R, \\ \rho_0^{\text{int}} &:= \bar{\Pi}^t : D_t F, \end{aligned} \right\} \tag{4.19}$$

whereby ρ_0^{ext} characterizes the total rate of working of mechanical actions on the body. This rate of working consists of the flux contribution $v \cdot \bar{\Pi}^t + KR$ and the source term $v \cdot \bar{b}_0 + K\mathcal{R}_0 - \nabla_X K \cdot R$. The internal mechanical power ρ_0^{int} consists exclusively of the production term for the kinetic energy as $\bar{\Pi}^t : D_t F$. The definition of the latter suggests the interpretation of the reduced momentum flux $\bar{\Pi}^t$ and the material time derivative of the deformation gradient $D_t F$ as work conjugate pairs. With the above abbreviations at hand, the balance of kinetic energy can be rewritten in a form which has been denoted as the local form: the ‘theorem of energy’ by Maugin (1993).

$$D_t K_0 = \rho_0^{\text{ext}} - \rho_0^{\text{int}}, \quad d_t K_t + \text{div}(K_t v) = \rho_t^{\text{ext}} - \rho_t^{\text{int}}. \tag{4.20}$$

The spatial version of the balance of kinetic energy (4.20)₂ follows naturally by applying the appropriate Piola transforms $K_0 = JK_t$, $\rho_0^{\text{ext}} = J\rho_t^{\text{ext}}$ and $\rho_0^{\text{int}} = J\rho_t^{\text{int}}$, along with Reynolds’s transport theorem (2.11).

(b) *Mass-specific version*

The mass-specific version of the balance of momentum is based on the mass-specific kinetic-energy density

$$K = \frac{1}{2}v \cdot v, \tag{4.21}$$

defining the quantity to be balanced as its partial derivative with respect to the spatial velocity v ,

$$p = \partial_v K = v. \tag{4.22}$$

The rate of change of the mass-specific momentum density p , i.e. the covariant spatial velocity, is balanced with the reduced momentum fluxes $\bar{\Pi}^t$ or $\bar{\sigma}^t$ and the reduced momentum sources \bar{b}_0 or \bar{b}_t . By subtracting the balance of mass (3.5) weighted by the momentum density p from the volume-specific momentum balance (4.7), we can derive the different versions of the mass-specific momentum balance,

$$\rho_0 D_t p = \text{Div } \bar{\Pi}^t + \bar{b}_0, \quad \rho_t d_t p + \rho_t v \cdot \nabla_x p = \text{div } \bar{\sigma}^t + \bar{b}_t. \tag{4.23}$$

The reduced momentum fluxes $\bar{\Pi}^t$ and $\bar{\sigma}^t$, which are related to the overall momentum fluxes Π^t and σ^t through $\bar{\Pi}^t = \Pi^t - p \otimes R$ and $\bar{\sigma}^t = \sigma^t - p \otimes r$, are determined by the closed- and open-system stress-vector contributions t_0^{closed} and \bar{t}_0^{open} or t_t^{closed} and \bar{t}_t^{open} , respectively, on the Neumann boundary,

$$\left. \begin{aligned} \bar{\Pi}^t \cdot N &= t_0^{\text{closed}} + \bar{t}_0^{\text{open}}, \\ \bar{\sigma}^t \cdot n &= t_t^{\text{closed}} + \bar{t}_t^{\text{open}}. \end{aligned} \right\} \tag{4.24}$$

while the reduced momentum sources \bar{b}_0 and \bar{b}_t are given as the sum of the classical closed-system volume force contributions b_0^{closed} or b_t^{closed} and the reduced open-system contributions \bar{b}_0^{open} or \bar{b}_t^{open} :

$$\left. \begin{aligned} \bar{b}_0 &= b_0^{\text{closed}} + \bar{b}_0^{\text{open}}, \\ \bar{b}_t &= b_t^{\text{closed}} + \bar{b}_t^{\text{open}}. \end{aligned} \right\} \tag{4.25}$$

Note that the mass-specific momentum balance (4.23) is free from all the explicit extra terms caused by the changes in mass. The influence of the open system manifests itself only implicitly through the prescribed boundary terms \bar{t}_0^{open} and \bar{t}_t^{open} and the prescribed volume sources \bar{b}_0^{open} and \bar{b}_t^{open} . The convective influence introduced through the $\rho_t v \cdot \nabla_x p$ term, however, is also present in the closed-system case.

Remark 4.3 (balance of angular momentum). The mass-specific angular-momentum density l is given as the vector product of the mass-specific momentum density p with the distance vector $a = \varphi - \varphi_0$:

$$l = a \times p. \tag{4.26}$$

Consequently, the mass-specific version of the balance of angular momentum follows from the vector product of the mass-specific momentum balance (4.23) with the distance vector a ,

$$a \times \rho_0 D_t p = a \times \text{Div } \bar{\Pi}^t + a \times \bar{b}_0. \tag{4.27}$$

By making use of the definition (4.26), the above equation can be rewritten as

$$\rho_0 D_t l = \text{Div}(a \times \bar{\Pi}^t) + a \times \bar{b}_0 - F \times \bar{\Pi}^t. \tag{4.28}$$

Again, the third term on the right-hand side, $-F \times \bar{\Pi}^t = 2[F \cdot \bar{\Pi}]^{\text{axl}}$, represents the production of the mass-specific angular momentum l . If we require the balance of angular momentum to represent an individual independent statement,

$$\rho_0 D_t l = \text{Div}(a \times \bar{\Pi}^t) + a \times \bar{b}_0, \tag{4.29}$$

this production term has to vanish identically. This condition thus reveals the symmetry requirements

$$F \cdot \bar{\Pi} = \bar{\Pi}^t \cdot F^t, \quad \bar{\sigma} = \bar{\sigma}^t. \tag{4.30}$$

The material and the spatial versions, (4.30)₁ and (4.30)₂, respectively, are related through the corresponding Piola transform $\bar{\Pi}^t = J\bar{\sigma}^t \cdot F^{-t}$. A comparison of the volume-specific statement (4.13) with its mass-specific counterpart (4.29) indicates that the in- or outflux of mass R or r produces an additional amount of angular momentum unless

$$F \cdot R \otimes p = p \otimes R \cdot F^t, \quad r \otimes p = p \otimes r, \tag{4.31}$$

i.e. the mass flux $F \cdot R$ or r is constitutively defined to be coaxial to the mass-specific momentum density p .

Remark 4.4 (balance of kinetic energy). To investigate the mass-specific version of the balance of kinetic energy, we need to evaluate the material time derivative of the mass-specific kinetic-energy density $K = \frac{1}{2}v \cdot v$, which can easily be derived by subtracting the weighted balance of mass (4.15)₂ from the material time derivative of the volume-specific kinetic-energy density K_0 given in equation (4.18) as

$$\rho_0 D_t K = D_t K_0 - K D_t \rho_0, \tag{4.32}$$

and thus

$$\rho_0 D_t K = \text{Div}(v \cdot \bar{\Pi}^t) + v \cdot \bar{b}_0^{\text{ext}} - \bar{\Pi}^t : D_t F. \tag{4.33}$$

Consequently, we can identify the mass-specific external and internal mechanical power, ρ_0^{ext} and ρ_0^{int} , respectively:

$$\left. \begin{aligned} \rho_0^{\text{ext}} &:= \rho_0^{\text{ext}} - K D_t \rho_0 = \text{Div}(v \cdot \bar{\Pi}^t) + v \cdot \bar{b}_0, \\ \rho_0^{\text{int}} &:= \rho_0^{\text{int}} = \bar{\Pi}^t : D_t F. \end{aligned} \right\} \tag{4.34}$$

It is worth noting that the difference of the mass- and volume-specific formulation manifests itself only in the definition of the external mechanical power $\rho_0^{\text{ext}} = \rho_0^{\text{ext}} - K D_t \rho_0$, while the mass-specific internal power is identical to its volume-specific counterpart as $\rho_0^{\text{int}} = \rho_0^{\text{int}}$. Consequently, the material and the spatial version of the mass-specific balance of kinetic energy take the formats

$$\rho_0 D_t K = \rho_0^{\text{ext}} - \rho_0^{\text{int}}, \quad \rho_t d_t K + \rho_t v \cdot \nabla_x K = \rho_t^{\text{ext}} - \rho_t^{\text{int}}, \tag{4.35}$$

whereby both formulations are related through the corresponding Piola transforms with $\rho_0^{\text{ext}} = J\rho_t^{\text{ext}}$ and $\rho_0^{\text{int}} = J\rho_t^{\text{int}}$ and the Euler theorem (2.4).

5. Balance of energy

The balance of total energy as a representation of the first law of thermodynamics balances the rate of change of the volume-specific total energy density E_0 or E_t as the sum of the kinetic and internal energy density $E_0 = K_0 + I_0$ or $E_t = K_t + I_t$ with the external power. In classical continuum mechanics of closed systems, this external power is composed of a purely mechanical contribution, ρ_0^{ext} or ρ_t^{ext} , and a non-mechanical thermal contribution, q_0^{ext} or q_t^{ext} . Therefore, the balance of energy is sometimes referred to as the ‘principle of interconvertibility of heat and mechanical work’, a notion which was known to Carnot in 1832 and experimentally verified by Joule in 1843. However, when dealing with open systems, we have to generalize the definition of the non-mechanical external power by including additional external open-system contributions in the definition of q_0^{ext} and q_t^{ext} (cf. Malvern 1969, §5.4).

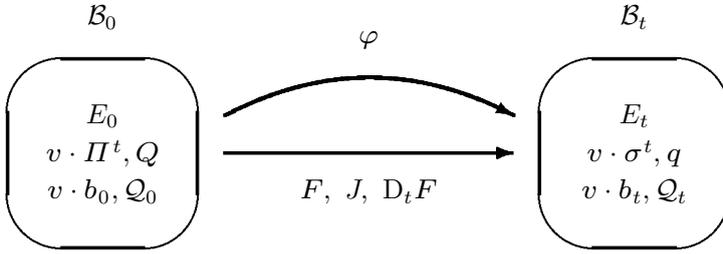


Figure 4. Balance of energy: energy densities, fluxes and sources.

(a) Volume-specific version

For the spatial-motion problem, the rate of change of the volume-specific total energy density $E_0 = \rho_0 E$ can be expressed in the form (cf. figure 4)

$$D_t E_0 = \text{Div}(v \cdot \bar{\Pi}^t - \bar{Q} + ER) + v \cdot \bar{b}_0 + \bar{Q}_0 + ER_0 - \nabla_X E \cdot R. \tag{5.1}$$

Thereby, in addition to the purely mechanical external power, P_0^{ext} , defined in equation (4.19), we have included the non-mechanical external power, q_0^{ext} , accounting for the classical thermal effects of the closed system and the additional open-system effects as an additional non-mechanical supply of energy,

$$q_0^{\text{ext}} := \text{Div}(-Q) + Q_0. \tag{5.2}$$

Similar to the mechanical power, the non-mechanical power consists of a flux and a source contribution, denoted by Q and Q_0 , respectively. The former is composed of the reduced outward non-mechanical energy flux \bar{Q} modified by the explicit extra flux due to the open system IR , while the latter is the sum of the reduced non-mechanical energy source \bar{Q}_0 , enhanced by the explicit effects of the open system IR_0 and $\nabla_X I \cdot R$:

$$\left. \begin{aligned} P_0^{\text{ext}} &:= \text{Div}(v \cdot \bar{\Pi}^t + KR) + v \cdot \bar{b}_0 + KR_0 - \nabla_X K \cdot R, \\ q_0^{\text{ext}} &:= \text{Div}(-\bar{Q} + IR) + \bar{Q}_0 + IR_0 - \nabla_X I \cdot R. \end{aligned} \right\} \tag{5.3}$$

Equation (5.1) can thus be reformulated in the concise form

$$D_t E_0 = P_0^{\text{ext}} + q_0^{\text{ext}}, \quad d_t E_t + \text{div}(E_t v) = P_t^{\text{ext}} + q_t^{\text{ext}}, \tag{5.4}$$

which, for the classical closed-system case, dates back to the early works of Duhem in 1892. Again, the spatial version (5.4)₂ follows from the appropriate Piola transforms $E_0 = JE_t$, $P_0^{\text{ext}} = JP_t^{\text{ext}}$, $q_0^{\text{ext}} = Jq_t^{\text{ext}}$, $Q = Jq \cdot F^{-t}$ and $\bar{Q} = J\bar{q} \cdot F^{-t}$, along with Reynolds's transport theorem (2.11). The definition of the non-mechanical energy fluxes Q and q parallels the introduction of the first Piola–Kirchhoff stress tensor Π and the Cauchy stress σ . On the Neumann boundary, the non-mechanical energy fluxes Q and q are given in terms of the normal projection of the classical heat flux densities q_0^{closed} and q_t^{closed} and the additional open-system contributions q_0^{open} and q_t^{open} :

$$\left. \begin{aligned} Q \cdot N &= q_0^{\text{closed}} + q_0^{\text{open}} q_0^{\text{open}} = \bar{q}_0^{\text{open}} - IR \cdot N, \\ q \cdot n &= q_t^{\text{closed}} + q_t^{\text{open}} q_t^{\text{open}} = \bar{q}_t^{\text{open}} - Ir \cdot n. \end{aligned} \right\} \tag{5.5}$$

Moreover, the non-mechanical energy sources \mathcal{Q}_0 and \mathcal{Q}_t can be understood as the sum of the classical heat source $\mathcal{Q}_0^{\text{closed}}$ and $\mathcal{Q}_t^{\text{closed}}$ and an additional non-mechanical energy source taking into account the nature of the open system $\mathcal{Q}_0^{\text{open}}$ and $\mathcal{Q}_t^{\text{open}}$,

$$\left. \begin{aligned} \mathcal{Q}_0 &= \mathcal{Q}_0^{\text{closed}} + \mathcal{Q}_0^{\text{open}} \mathcal{Q}_0^{\text{open}} = \bar{\mathcal{Q}}_0^{\text{open}} + I\mathcal{R}_0 - \nabla_x I \cdot R, \\ \mathcal{Q}_t &= \mathcal{Q}_t^{\text{closed}} + \mathcal{Q}_t^{\text{open}} \mathcal{Q}_t^{\text{open}} = \mathcal{Q}_t^{\text{open}} + I\mathcal{R}_t - \nabla_x I \cdot r. \end{aligned} \right\} \tag{5.6}$$

In formal analogy to the definition of the momentum quantities, the expressions in terms of R, r, \mathcal{R}_0 and \mathcal{R}_t take into account the part of the newly added mass that carries the same amount of non-mechanical energy as the original substrate, while the additional open-system terms $\bar{q}_0^{\text{open}}, \bar{q}_t^{\text{open}}, \bar{\mathcal{Q}}_0^{\text{open}}$ and $\bar{\mathcal{Q}}_t^{\text{open}}$ account for a possible difference in non-mechanical energy.

Remark 5.1 (balance of internal energy). For further thermodynamical considerations, it proves convenient to consider the volume-specific internal energy density $I_0 = E_0 - K_0$ or $I_t = E_t - K_t$ given as the difference of the corresponding total energy density and the kinetic-energy density. Consequently, the two versions of the balance of internal energy follow from subtracting the balance of kinetic energy (4.20) from the total energy balance (5.4):

$$D_t I_0 = \rho_0^{\text{int}} + q_0^{\text{ext}}, \quad d_t I_t + \text{div}(I_t v) = \rho_t^{\text{int}} + q_t^{\text{ext}}. \tag{5.7}$$

(b) *Mass-specific version*

The mass-specific counterpart of the equations derived above balances the mass-specific energy density $E = E_0/\rho_0$ with the mass-specific external mechanical power ρ_0^{ext} introduced in (4.34) and the mass-specific non-mechanical power q_0^{ext} as

$$q_0^{\text{ext}} := q_0^{\text{ext}} - ID_t \rho_0 = -\text{Div } \bar{Q} + \bar{\mathcal{Q}}_0. \tag{5.8}$$

The corresponding balance equations,

$$\rho_0 D_t E = \rho_0^{\text{ext}} + q_0^{\text{ext}}, \quad \rho_t d_t E + \rho_t v \cdot \nabla_x E = \rho_t^{\text{ext}} + q_t^{\text{ext}}, \tag{5.9}$$

follow from subtracting the corresponding balance of mass (3.5) weighted by the total energy E from the volume-specific energy balance (5.4). The spatial version, (5.9)₂, can be derived by applying the corresponding Piola transforms with $\rho_0^{\text{ext}} = J\rho_t^{\text{ext}}$ and $q_0^{\text{ext}} = Jq_t^{\text{ext}}$ and the Euler theorem (2.4). Again, we can relate the reduced energy fluxes \bar{Q} and \bar{q} defined through $\bar{Q} = Q - IR$ and $\bar{q} = q - Ir$ to the classical heat flux q_0^{closed} or q_t^{closed} and the energy flux caused by additional effects of the open system \bar{q}_0^{open} and \bar{q}_t^{open} :

$$\left. \begin{aligned} \bar{Q} \cdot N &= q_0^{\text{closed}} + \bar{q}_0^{\text{open}}, \\ \bar{q} \cdot n &= q_t^{\text{closed}} + \bar{q}_t^{\text{open}}. \end{aligned} \right\} \tag{5.10}$$

Moreover, the reduced non-mechanical energy sources $\bar{\mathcal{Q}}_0$ and $\bar{\mathcal{Q}}_t$ are given as the sum of the classical heat source of a closed system $\mathcal{Q}_0^{\text{closed}}$ and $\mathcal{Q}_t^{\text{closed}}$ and the additional open-system contribution to the energy $\bar{\mathcal{Q}}_0^{\text{open}}$ and $\bar{\mathcal{Q}}_t^{\text{open}}$:

$$\left. \begin{aligned} \bar{\mathcal{Q}}_0 &= \mathcal{Q}_0^{\text{closed}} + \bar{\mathcal{Q}}_0^{\text{open}}, \\ \bar{\mathcal{Q}}_t &= \mathcal{Q}_t^{\text{closed}} + \bar{\mathcal{Q}}_t^{\text{open}}. \end{aligned} \right\} \tag{5.11}$$

Again, as opposed to the formulation developed by Epstein & Maugin (2000), the mass-specific format is free from all the explicit extra terms caused by changes in mass and thus resembles the balance of energy known from classical mechanics.

Remark 5.2 (balance of internal energy). A reduction to the balance of internal energy $I = E - K$ follows from subtracting the balance of kinetic energy (4.35) from the balance of total energy (5.9):

$$\rho_0 D_t I = \rho_0^{\text{int}} + \mathbf{q}_0^{\text{ext}}, \quad \rho_t d_t I + \rho_t \mathbf{v} \cdot \nabla_x I = \rho_t^{\text{int}} + \mathbf{q}_t^{\text{ext}}. \tag{5.12}$$

6. Balance of entropy

The first law of thermodynamics in the form of the balance of energy expresses the interconvertibility of heat and work. However, the balance of energy itself does not place any restrictions on the direction of the thermodynamical process. The second law of thermodynamics, the balance of entropy, postulates the existence of an absolute temperature and of a specific entropy as a state function. Through the internal production of the latter, which is required to either vanish for reversible processes or be strictly positive for irreversible processes, a direction is imposed on the thermodynamical process. Recall that, when dealing with open systems, a fixed material volume, \mathcal{B}_0 , is allowed to constantly gain or lose mass. Open systems naturally exhibit an additional entropy flux and entropy source caused by the added mass as pointed out earlier in the famous monograph by Schrödinger (1944, § 6) as well as by Malvern (1969, § 5.6) or also recently by Epstein & Maugin (2000). The influence of changes in mass on the entropy is twofold. On the one hand, it is reflected through the explicit open-system entropy flux SR and the related source terms $S\mathcal{R}_0$ and $-\nabla_X S \cdot R$. On the other hand, we will introduce the reduced entropy flux and source, \bar{H} and $\bar{\mathcal{H}}_0$, respectively, which in turn split into the extra non-mechanical energy terms, \bar{Q} and $\bar{\mathcal{Q}}_0$, divided by the absolute temperature θ and an extra entropy flux and source S and \mathcal{S}_0 . While the former parallel the introduction of the entropy flux and source in classical closed-system thermodynamics, the contributions S and \mathcal{S}_0 account for the difference in entropy of the added mass and the original substrate.

Remark 6.1 (balance of entropy versus entropy inequality). In the related literature, the entropy is often introduced through the entropy inequality. For the sake of analogy, we will treat the entropy as a balance quantity in the following. Its evolution is thus balanced with the sum of the external and internal entropy production, whereby the latter is constrained to be non-negative throughout. In the case of closed-system thermodynamics, this approach has been followed, for example, by Truesdell & Toupin (1960, §§ 256 and 257), Haupt (2000, § 3.3) or Liu (2002, § 5).

(a) Volume-specific version

The balance of entropy balances the volume-specific entropy density $S_0 = \rho_0 S$ with the external entropy input h_0^{ext} and the internal entropy production h_0^{int} . Thereby, the former consists of the entropy flux H across the material surface $\partial\mathcal{B}_0$ and the entropy source \mathcal{H}_0 in the material domain \mathcal{B}_0 (cf. figure 5),

$$h_0^{\text{ext}} := \text{Div}(-H) + \mathcal{H}_0. \tag{6.1}$$

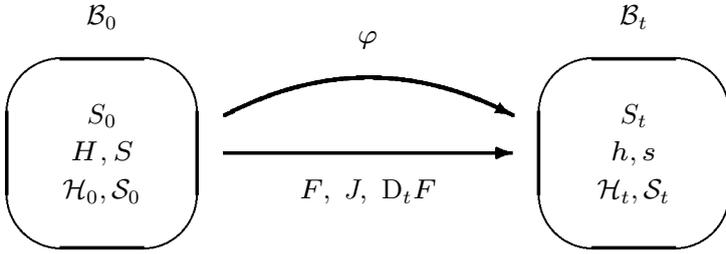


Figure 5. Balance of entropy: entropy densities, fluxes and sources.

The external entropy flux H is introduced as the sum of the reduced external entropy flux \bar{H} , enhanced by the explicit open-system contribution SR . Accordingly, the external entropy source \mathcal{H}_0 consists of the reduced entropy source $\bar{\mathcal{H}}_0$ modified by additional terms $S\mathcal{R}_0$ and $-\nabla_X S \cdot R$ accounting for the explicit open-system contribution to the entropy supply:

$$\left. \begin{aligned} h_0^{\text{ext}} &:= \text{Div}(-\bar{H} + SR) + \bar{\mathcal{H}}_0 + S\mathcal{R}_0 - \nabla_X S \cdot R, \\ h_0^{\text{int}} &\geq 0. \end{aligned} \right\} \tag{6.2}$$

Just like in classical thermodynamics of closed systems, the internal entropy production h_0^{int} is required to be point-wise non-negative. The balance of entropy can thus be expressed in the following form:

$$D_t S_0 = h_0^{\text{ext}} + h_0^{\text{int}}, \quad d_t S_t + \text{div}(S_t v) = h_t^{\text{ext}} + h_t^{\text{int}}. \tag{6.3}$$

Again, the material and the spatial version are related through the corresponding Piola transforms $S_0 = JS_t$, $h_0^{\text{ext}} = Jh_t^{\text{ext}}$, $h_0^{\text{int}} = Jh_t^{\text{int}}$, $H = Jh \cdot F^{-t}$ and $\bar{H} = J\bar{h} \cdot F^{-t}$, in combination with Reynolds’s transport theorem. Note that, alternatively, the balance of entropy, which is primarily nothing but a formal definition of the entropy production, can be recast into the inequality $D_t S_0 - h_0^{\text{ext}} \geq 0$. This condition, which is typically referred to as ‘postulate of irreversibility’ in classical thermodynamics (see Truesdell & Toupin 1960, §258), induces a direction to the thermodynamic process. Next, we will introduce Neumann boundary conditions for the spatial-motion Kirchhoff and Cauchy type entropy flux H and h in terms of the classical closed-system entropy flux contribution h_0^{closed} or h_t^{closed} and the additional open-system contribution h_0^{open} or h_t^{open} :

$$\left. \begin{aligned} H \cdot N &= h_0^{\text{closed}} + h_0^{\text{open}}, & h_0^{\text{open}} &= \bar{h}_0^{\text{open}} - SR \cdot N, \\ h \cdot n &= h_t^{\text{closed}} + h_t^{\text{open}}, & h_t^{\text{open}} &= \bar{h}_t^{\text{open}} - Sr \cdot n. \end{aligned} \right\} \tag{6.4}$$

Accordingly, the entropy sources \mathcal{H}_0 and \mathcal{H}_t are introduced as the sum of the classical entropy source of the closed system $\mathcal{H}_0^{\text{closed}}$ or $\mathcal{H}_t^{\text{closed}}$ and the additional entropy source accounting for the nature of the open system $\mathcal{H}_0^{\text{open}}$ or $\mathcal{H}_t^{\text{open}}$,

$$\left. \begin{aligned} \mathcal{H}_0 &= \mathcal{H}_0^{\text{closed}} + \mathcal{H}_0^{\text{open}}, & \mathcal{H}_0^{\text{open}} &= \bar{\mathcal{H}}_0^{\text{open}} + S\mathcal{R}_0 - \nabla_X S \cdot R, \\ \mathcal{H}_t &= \mathcal{H}_t^{\text{closed}} + \mathcal{H}_t^{\text{open}}, & \mathcal{H}_t^{\text{open}} &= \bar{\mathcal{H}}_t^{\text{open}} + S\mathcal{R}_t - \nabla_x S \cdot r. \end{aligned} \right\} \tag{6.5}$$

(b) *Mass-specific version*

The mass-specific counterpart of the above equations states that the rate of change of the mass-specific entropy $S = S_0/\rho_0$ is in equilibrium with the mass-specific external entropy input h_0^{ext} and the mass-specific internal entropy production h_0^{int} , which are introduced in the following way:

$$\left. \begin{aligned} h_0^{\text{ext}} &:= h_0^{\text{ext}} - S D_t \rho_0 = -\text{Div } \bar{H} + \bar{\mathcal{H}}_0, \\ h_0^{\text{int}} &:= h_0^{\text{int}} \geq 0. \end{aligned} \right\} \tag{6.6}$$

The resulting material and spatial version of the balance of entropy,

$$\rho_0 D_t S = h_0^{\text{ext}} + h_0^{\text{int}}, \quad \rho_t d_t S + \rho_t v \cdot \nabla_x S = h_t^{\text{ext}} + h_t^{\text{int}}, \tag{6.7}$$

which can be derived by subtracting S times the balance of mass (3.5) from the volume-specific balance of entropy (6.3), are related via the appropriate Piola transforms $h_0^{\text{ext}} = J h_t^{\text{ext}}$ and $h_0^{\text{int}} = J h_t^{\text{int}}$ and the Euler theorem (2.4). Moreover, we can relate the reduced entropy fluxes \bar{H} and \bar{h} defined through $\bar{H} = H - SR$ and $\bar{h} = h - Sr$ to the classical entropy flux of the closed system h_0^{closed} or h_t^{closed} , and the entropy flux caused by additional effects of the open system \bar{h}_0^{open} or \bar{h}_t^{open} ,

$$\left. \begin{aligned} \bar{H} \cdot N &= h_0^{\text{closed}} + \bar{h}_0^{\text{open}}, \\ \bar{h} \cdot n &= h_t^{\text{closed}} + \bar{h}_t^{\text{open}}. \end{aligned} \right\} \tag{6.8}$$

Accordingly, the reduced entropy sources $\bar{\mathcal{H}}_0 = \mathcal{H}_0 - S\mathcal{R}_0 + \nabla_x S \cdot R$ and $\bar{\mathcal{H}}_t = \mathcal{H}_t - S\mathcal{R}_t + \nabla_x S \cdot r$ are given as the sum of the classical closed-system entropy source $\mathcal{H}_0^{\text{closed}}$ or $\mathcal{H}_t^{\text{closed}}$, and the additional open-system contribution to the entropy source $\mathcal{H}_0^{\text{open}}$ or $\mathcal{H}_t^{\text{open}}$,

$$\left. \begin{aligned} \bar{\mathcal{H}}_0 &= \mathcal{H}_0^{\text{closed}} + \bar{\mathcal{H}}_0^{\text{open}}, \\ \bar{\mathcal{H}}_t &= \mathcal{H}_t^{\text{closed}} + \bar{\mathcal{H}}_t^{\text{open}}. \end{aligned} \right\} \tag{6.9}$$

Remark 6.2 (dissipation inequality). For further elaboration, it proves convenient to set up relations between the reduced entropy flux \bar{H} and the reduced non-mechanical energy flux \bar{Q} , and between the reduced entropy source $\bar{\mathcal{H}}_0$ and the reduced non-mechanical energy source $\bar{\mathcal{Q}}_0$, in terms of the absolute temperature θ , an extra entropy flux S and an extra entropy source \mathcal{S}_0 :

$$\bar{H} = \frac{1}{\theta} \bar{Q} + S, \quad \bar{\mathcal{H}}_0 = \frac{1}{\theta} \bar{\mathcal{Q}}_0 + \mathcal{S}_0. \tag{6.10}$$

The above equations can be understood as a generalization of the ideas of Cowin & Hegedus (1976), who have suggested including the additional entropy source \mathcal{S}_0 accounting for changes in entropy caused by changes in mass that are not considered implicitly through the changes in energy $\bar{\mathcal{Q}}_0$. Both the additional entropy flux S and the entropy source \mathcal{S}_0 , which we shall summarize in the term $\mathcal{S}_0 = -\text{Div } S + \mathcal{S}_0$ in the following, have to be determined constitutively. These additional terms can be understood as an explicit representation of the exchange of entropy with the ‘outside world’. We now turn to the evaluation of the above-stated second law of thermodynamics by recasting it into an appropriate form of the dissipation inequality, a statement that places further restrictions on the form of the constitutive response

functions. For this purpose, we shall interpret the internal entropy production $\frac{h_{\text{int}}}{\theta}$ as a measure for the degree of irreversibility introducing the dissipation rate d_0 as the internal entropy production weighted by the absolute temperature as $d_0 := \theta \frac{h_{\text{int}}}{\theta} \geq 0$. With the help of the balance of entropy (6.7)₁, the relations (6.10) and the balance of internal energy (5.12)₁, the dissipation rate can be reformulated to yield the Clausius–Duhem inequality in an internal energy based fashion,

$$d_0 = \rho_0^{\text{int}} - \rho_0 D_t [I - \theta S] - \rho_0 S D_t \theta - s_0 \theta - \bar{Q} \cdot \nabla_X \ln \theta \geq 0. \tag{6.11}$$

By making use of the appropriate Legendre–Fenchel transform introducing the Helmholtz free energy $\Psi = I - \theta S$, we end up with the classical free-energy-based version of the Clausius–Duhem inequality,

$$d_0 = \bar{\Pi}^t : D_t F - \rho_0 D_t \Psi - \rho_0 S D_t \theta - s_0 \theta - \bar{Q} \cdot \nabla_X \ln \theta \geq 0, \tag{6.12}$$

which is particularly useful when the temperature, θ , rather than the entropy, S , is used as the independent variable. In classical thermodynamics, the Clausius–Duhem inequality (6.12) is typically decomposed into a local and a conductive contribution d_0^{loc} and d_0^{con} ,

$$d_0^{\text{loc}} = \bar{\Pi}^t : D_t F - \rho_0 D_t \Psi - \rho_0 S D_t \theta - s_0 \theta \geq 0, \quad d_0^{\text{con}} = -\bar{Q} \cdot \nabla_X \ln \theta \geq 0, \tag{6.13}$$

whereby the local term $d_0^{\text{loc}} \geq 0$ represents the Clausius–Planck inequality for open systems, while the remaining conductive term $d_0^{\text{con}} \geq 0$ is typically referred to as a Fourier inequality. As a sufficient condition for $d_0 \geq 0$, both inequalities are required to hold separately. In what follows, we shall apply the dissipation inequality (6.13) to derive constitutive equations for the reduced momentum flux $\bar{\Pi}^t$ and the entropy S . In addition, the evaluation of the dissipation inequality places further restrictions on the extra entropy exchange s_0 . The underlying procedure will be highlighted in detail for the simple model problem of thermo-hyperelasticity in the following section.

Remark 6.3. Note that, at this stage, the introduction of the reduced entropy flux and source $\bar{H} = \bar{Q}/\theta + S$ and $\bar{\mathcal{H}}_0 = \bar{Q}_0/\theta + \mathcal{S}_0$, as introduced in equations (6.10), is a mere constitutive assumption. Nevertheless, for particular constitutive-model problems, the postulated relations can be verified through the evaluation of the dissipation inequality according to Müller (1973) and Liu (1972) (see also Liu 2002). It will turn out that, in most cases, equations (6.10) are justified with the trivial solution $S = \mathbf{0}$ and $\mathcal{S}_0 = 0$. However, assuming this result from the very outset might be too restrictive for complex constitutive models, as also pointed out by Epstein & Maugin (2000).

7. Thermo-hyperelasticity

We are now in a position to exploit the second law of thermodynamics in the form of the Clausius–Duhem inequality along the lines of Coleman & Noll (1963). The straightforward evaluation of the local part of the dissipation inequality in the form of the Clausius–Planck inequality (6.13)₁ will result in the definition of the reduced momentum flux $\bar{\Pi}$ and the mass-specific entropy density S . Its conductive supplement (6.13)₂, the Fourier inequality, suggests the definition of the reduced non-mechanical energy flux \bar{Q} along the lines of the classical linear heat conduction introduced by Fourier in 1822. Finally, the mass flux R will be introduced constitutively

in the context of classical linear mass diffusion according to Fick's law. Here, we will thus restrict ourselves to a thermo-hyperelastic-model problem for which all the dissipation is caused exclusively by heat conduction and possibly by an additional open-system contribution of the 'outside world'. In what follows, we shall make use of the multiplicative decomposition of the free energy Ψ_0 ,

$$\Psi_0 = \rho_0 \Psi. \tag{7.1}$$

Thereby, the mass-specific free-energy density Ψ is expressed in terms of the material density ρ_0 , the deformation gradient F and the absolute temperature θ with a possible explicit dependence on the material placement X . Within the thermodynamics of open systems, the material density ρ_0 is allowed to vary in space, and time is thus introduced as function of the material placement X and the time t :

$$\Psi = \Psi(\rho_0, F, \theta; X), \quad \rho_0 = \rho_0(X, t). \tag{7.2}$$

Consequently, the material time derivative of the free-energy density is formally given in the form:

$$D_t \Psi = D_{\rho_0} \Psi D_t \rho_0 + D_F \Psi : D_t F + D_\theta \Psi D_t \theta. \tag{7.3}$$

The evaluation of the Clausius–Planck inequality (6.13)₁,

$$d_0^{loc} = -\rho_0 D_{\rho_0} \Psi D_t \rho_0 + [\bar{\Pi}^t - \rho_0 D_F \Psi] : D_t F - [\rho_0 S + \rho_0 D_\theta \Psi] D_t \theta - S_0 \theta \geq 0, \tag{7.4}$$

defines the reduced first Piola–Kirchhoff stress tensor $\bar{\Pi}^t$ and the mass-specific entropy S as thermodynamically conjugate variables to the deformation gradient F and the absolute temperature θ :

$$\bar{\Pi}^t = \rho_0 D_F \Psi, \quad S = -D_\theta \Psi. \tag{7.5}$$

As in Cowin & Hegedus (1976), we are left with a reduced inequality of the form

$$d_0^{loc} = -\rho_0 D_{\rho_0} \Psi D_t \rho_0 - S_0 \theta \geq 0. \tag{7.6}$$

In biomechanics, the simplest choice for the free-energy function Ψ for cellular materials such as open-pored biological tissues is based on the classical isotropic Neo-Hookean-type free-energy function weighted by the actual relative density $[\rho_0/\rho_0^*]^n$ (see, for example, Carter & Hayes 1977; Gibson & Ashby 1997),

$$\Psi = \left[\frac{\rho_0}{\rho_0^*} \right]^{[n-1]} \frac{1}{\rho_0^*} \left[\frac{1}{2} \lambda \ln^2 J + \frac{1}{2} \mu [b : \mathbf{1} - 3 - 2 \ln J] \right]. \tag{7.7}$$

Here, λ and μ denote the classical Lamé constants and n is an additional exponent usually allowed to vary between $1 \leq n \leq 3.5$. A selection of more advanced free-energy functions for orthotropic biological tissues can be found, for example, in the recent collection of publications by Cowin & Humphrey (2001). The derivatives of the free energy Ψ with respect to the material density ρ_0 and the deformation gradient F take the format

$$\left. \begin{aligned} D_{\rho_0} \Psi &= [n-1] \left[\frac{\rho_0}{\rho_0^*} \right]^{[n-2]} \left[\frac{1}{\rho_0^*} \right]^2 \left[\frac{1}{2} \lambda \ln^2 J + \frac{1}{2} \mu [b : \mathbf{1} - 3 - 2 \ln J] \right], \\ D_F \Psi &= \left[\frac{\rho_0}{\rho_0^*} \right]^{[n-1]} \left[\frac{1}{\rho_0^*} \right] [\mu F + [\lambda \ln J - \mu] F^{-t}], \end{aligned} \right\} \tag{7.8}$$

whereby the first derivative can alternatively be expressed as $D_{\rho_0}\Psi = [n - 1]\Psi/\rho_0$. According to equation (7.5), the reduced first Piola–Kirchhoff stress tensor

$$\bar{\Pi}^t = \left[\frac{\rho_0}{\rho_0^*} \right]^n [\mu F + [\lambda \ln J - \mu] F^{-t}] \quad (7.9)$$

can be understood as the classical Neo-Hookean stress tensor weighted by the actual relative density $[\rho_0/\rho_0^*]^n$. The reduced dissipation inequality,

$$-[n - 1]\Psi[\text{Div } R + \mathcal{R}_0] + \theta[\text{Div } S - \mathcal{S}_0] \geq 0, \quad (7.10)$$

places implicit restrictions on the dissipation generated by the density evolution $D_t\rho_0$ through the mass flux R and the mass source \mathcal{R}_0 . This amount of dissipation has at least to be compensated by an appropriate constitutive assumption for the extra external entropy input, \mathcal{S}_0 , through the extra entropy flux S and the extra entropy source \mathcal{S}_0 , e.g.

$$S = [n - 1]\Psi \frac{1}{\theta} R, \quad \mathcal{S}_0 = -[n - 1]\Psi \frac{1}{\theta} \mathcal{R}_0. \quad (7.11)$$

Similar to the context of chemomechanics, the flux r or R is usually related to the spatial or material gradient of the density $\nabla_x \rho_0$ or $\nabla_X \rho_0$ as

$$r = R_0 b \cdot \nabla_x \rho_0, \quad R = r_t B \cdot \nabla_X \rho_0, \quad (7.12)$$

in analogy to Fick's law for concentrations. Here, R_0 and r_t denote the mass-conduction coefficient, introducing either a materially or a spatially isotropic response. In the context of biomechanics, we typically find variations of the constitutive equation

$$\mathcal{R}_0 = \left[\frac{\rho_0}{\rho_0^*} \right]^{-m} \Psi_0 - \Psi_0^* \quad (7.13)$$

for the mass source \mathcal{R}_0 , where ρ_0^* and Ψ_0^* denote the reference density and the reference free energy, respectively, while m is an additional exponent that is commonly chosen to $m > n$ (see Harrigan & Hamilton 1993). Finally, the evaluation of the Fourier inequality (6.13)₂ as $\mathcal{D}_0^{\text{con}} = -\bar{Q} \cdot \nabla_X \ln \theta \geq 0$ suggests the definition of the mass-specific non-mechanical energy flux \bar{q} or \bar{Q} according to Fourier's law as

$$\bar{q} = -K_0 b \cdot \nabla_x \theta, \quad \bar{Q} = -k_t B \cdot \nabla_X \theta, \quad (7.14)$$

with K_0 and k_t denoting the materially or spatially isotropic conductivity. In order to *a priori* guarantee the satisfaction of the Fourier inequality (6.13)₂, the conductivity is required to be non-negative, $K_0 \geq 0$ and $k_t \geq 0$.

8. Conclusion

We have presented a general framework for the thermodynamics of open systems. The derived field equations are believed to be particularly useful in biomechanical or chemomechanical applications where attention is confined to one individual subsystem of the overall matter present. Due to the fact that this open subsystem is allowed to constantly gain or lose mass, the balance of mass had to be enhanced by additional surface and volume terms reflecting the interaction with the 'outside world'. Since the newly created mass carries a particular amount of momentum,

energy and entropy, all the other balance equations had to be reformulated as well. To clarify the influence of the changes in mass, we have introduced the notions of ‘volume-specific’ and ‘mass-specific’ formats. The former accounts for the total influence of the changes in mass through explicit mass-dependent and additional implicit open-system contributions. The latter, however, is free from all the mass-dependent extra terms and thus takes the familiar structure known from classical continuum thermodynamics. The mass-specific format is believed to be particularly useful, since it parallels the framework of the closed-system case. Consequently, permissible constitutive relations can be derived from the mass-specific version of the dissipation inequality. The underlying procedure has been illustrated for the model problem of thermo-hyperelasticity.

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