

Chapter 2

Balance Equations in Continuum Physics

An equation means nothing to me unless it expresses a thought of God.

— Srinivasa Ramanujan, Quotations by 60 Greatest Indians

In this chapter, we present the basic equations of continuum physics both in global and local formulations. The local balance laws together with the global Clausius–Duhem inequality define the class of admissible thermodynamic processes. Boundary conditions and discontinuities appear as prominent issues. We give a few examples of constitutive equations for the stress tensor and for the transport fluxes. A set of worked-out practical modeling scenarios is emphasized.

2.1 Basic Notions

2.1.1 Notation, Body and Configurations, Coordinates

Throughout this chapter, we use scalars in \mathbb{R} (like m, ρ, θ), vectors in \mathbb{R}^d ($d \in \{1, 2, 3\}$) (like \mathbf{x}, \mathbf{v}), and tensors in $\mathbb{R}^d \times \mathbb{R}^d$ ($d \in \{1, 2, 3\}$) (like $\mathbb{F}, \mathbb{I}, \mathbb{T}$).

Sets will typically refer to either bodies or configurations. A material body is denoted by \mathcal{B} , while $\Omega = \Omega(t)$ is the corresponding momentary configuration at time $t \in S$. Here $S := (0, T_{fin})$ denotes the observation time interval with T_{fin} being the final observation time. We denote by $\Omega' = \Omega'(t)$ the momentary configuration of a material partial volume element, i.e., $\Omega'(t) \subset \Omega(t)$.

The reference configuration is $\Omega_R \subset \mathbb{R}^d$. The choice of Ω_R is in principle arbitrary, free to choose. For instance, for the rigid-body motion $\Omega_R = \Omega(0)$, for an elastic body Ω_R is the undeformed configuration, while for a flow Ω_R is the momentary configuration at the current time t . We also use $\Sigma_R \subset \mathbb{R}^{d-1}$ with $\Sigma_R \subset \Omega_R$.

The relation $\mathcal{P} \in \mathcal{B}$ points out a material point \mathcal{P} of the body \mathcal{B} . To describe its momentary position at time t , we use the Eulerian coordinates $\mathbf{x}(t) = \mathbf{x}(\mathcal{P}, t) \in \Omega(t)$. The Lagrangian coordinates of the same point are denoted here by $\xi = \xi(\mathcal{P}) \in \Omega_R$. The mapping $\mathcal{L}_t : \Omega_R \rightarrow \Omega(t)$ by $\mathbf{x}(t) = \mathcal{L}_t(\xi, t)$ models the motion of $\mathcal{P} \in \mathcal{B}$ from ξ to \mathbf{x} . Assume \mathcal{L}_t to be a C^2 diffeomorphism from $\bar{\Omega}_R$ onto $\bar{\Omega}(t)$.

With these notations at hand, the tensor $\mathbb{F} := \partial \mathcal{L}_t(\xi, t) / \partial \xi = \partial \mathbf{x} / \partial \xi$ is called the deformation gradient, while $\mathbf{v} = \partial \mathcal{L}_t(\xi, t) / \partial t = \partial \mathbf{x} / \partial t$ represents the velocity of \mathcal{P} at the current time t .

In Eulerian formulation, the (local or partial) time derivative of a function $f = \bar{f}(\mathbf{x}, t)$ is $\partial f / \partial t = \partial \bar{f} / \partial t$. In Lagrangian formulation, the material time derivative of a function $f = \hat{f}(\xi, t)$ is $Df / Dt = \partial \hat{f} / \partial t$. Note that the functions \bar{f} and \hat{f} represent f in the two systems of coordinates.

In this chapter as well as in Chap. 3, the (d -dimensional) volume measure is denoted by dx , $d\sigma$ points out the corresponding surface (area) measure, while μ_m represents the mass measure. Occasionally, we use λ as an alternative notation for the volume measure dx . By the introduction of the measure μ_m , we actually mean that the density ρ of the body is introduced as the Radon-Nikodym derivative $\rho := \frac{d\mu_m}{dx}$. All integrals should be seen in the sense of Lebesgue.

2.2 Global Balance Laws

The following five global balance laws serve as postulates for the theory of continuous media. In all these formulations, $\Omega'(t)$ is the configuration of an arbitrary partial volume (sub-body) \mathcal{B}' of \mathcal{B} . We postulate global balance laws for: *mass*, *linear momentum*, *angular momentum*, *energy*, and *entropy* as follows:

(i) *mass*

$$\frac{d}{dt} m(\Omega'(t), t) = 0 \quad (2.1)$$

for all $\Omega'(t) \subset \Omega(t)$, where $m(t)$ denotes the total mass within $\Omega'(t)$, i.e.,

$$m(\Omega'(t), t) = \int_{\Omega'(t)} d\mu_m = \int_{\Omega'(t)} \rho dx$$

with $\rho(t, \mathbf{x})$ being the density. In other words, in the absence of internal mass production terms, the total mass of any material partial volume is conserved. See further Sect. 2.3.1.

(ii) *linear momentum*

For every part $\Omega'(t) \subset \Omega(t)$, we have

$$\frac{d}{dt} \ell(\Omega'(t), t) = \mathbf{F}, \quad (2.2)$$

where the *linear momentum* is denoted by

$$\ell(\Omega'(t), t) := \int_{\Omega'(t)} \mathbf{v} \rho dx.$$

In other words, the change in time of the total linear momentum ℓ of \mathcal{B}' is equal to the force \mathbf{F} exerted on \mathcal{B}' . The force \mathbf{F} consists of the contribution of the internal body forces (per unit of volume) $\rho \mathbf{f}^b$ and contact or surface forces (per unit of area) \mathbf{t} acting on the boundary $\partial \mathcal{B}'$ of \mathcal{B}' . Here \mathbf{t} is the so-called stress vector. See further Sects. 2.3.2.1 and 2.3.2.2.

(iii) *angular momentum or moment of momentum*

For every part $\Omega'(t) \subset \Omega(t)$, we have

$$\frac{d}{dt} \alpha(\Omega'(t), t) = \mathbf{M}, \quad (2.3)$$

where the *angular momentum* is denoted by

$$\alpha(\Omega'(t), t) := \int_{\Omega'(t)} \mathbf{x} \times \mathbf{v} \rho dx.$$

In other words, the change in time of the total angular momentum α of \mathcal{B}' is equal to the moment \mathbf{M} of the force \mathbf{F} exerted on \mathcal{B}' . See further Sect. 2.3.6.

(iv) *energy*

The change in time of the total energy within \mathcal{B}' (i.e., the kinetic energy K and internal energy E) is equal to the rate of work, say P , done by both the body force and the contact force, plus the heat supply Q from internal heat production and heat fluxes across the boundary of \mathcal{B}' , so for every part $\Omega'(t) \subset \Omega(t)$, we have

$$\frac{d}{dt} (K(t) + E(t)) = P(t) + Q(t), \quad (2.4)$$

where

$$K(t) := \int_{\Omega'(t)} \frac{|\mathbf{v}|^2}{2} d\mu_m = \int_{\Omega'(t)} \frac{|\mathbf{v}|^2}{2} \rho dx, \quad (2.5)$$

$$E(t) := \int_{\Omega'(t)} e d\mu_m = \int_{\Omega'(t)} e \rho dx, \quad (2.6)$$

$$P(t) := \int_{\partial\Omega'} \mathbf{v} \cdot (\mathbb{T}\mathbf{n}) d\sigma + \int_{\Omega'} \vec{f} \cdot \vec{v} \rho dx, \quad (2.7)$$

$$Q(t) := \int_{\Omega'} f_{Heat} \rho dx + \int_{\partial\Omega'(t)} \mathbf{q} \cdot \mathbf{n} d\sigma. \quad (2.8)$$

In (2.6), e represents the inner energy density. The first term in $Q(t)$ accounts for the heat source. The measure μ_m entering the definition of $K(t)$ and $E(t)$ is just the mass measure associated to the material body \mathcal{B} . See further Sect. 2.3.5.

(v) *entropy*

The entropy increase within \mathcal{B} is greater than or equal to the internal entropy supply (internal heat source over θ , the absolute temperature) plus the entropy flux across the boundary of \mathcal{B}' , i.e.,

$$\frac{d}{dt} \left(\int_{\Omega'(t)} s d\mu_m \right) \geq \int_{\Omega'(t)} \frac{f_{Heat}}{\theta} d\mu_m - \int_{\partial\Omega'(t)} \frac{\mathbf{q} \cdot \mathbf{n}}{\theta} d\sigma. \quad (2.9)$$

Here s represents the entropy density. See further Sect. 2.3.7.

It is worth noting that the mass, the linear, and angular momentum as well as the energy and the entropy are all extensive quantities. As a matter of fact, global balance laws can only be written in terms of extensive quantities. The intensive quantities will be subject to local balance laws as we see next.

2.3 Local Balance Laws

Based on the global laws of the preceding section, local equations (partial differential equations and inequations) and boundary conditions can be derived. We present some of them here without too many details. More information can be found in the standard literature; see e.g. [Gur81, vdV09, TM05, GS08]. In all these derivations, Reynolds Transport Theorem is used; see Theorem 2.1 for the statement and proof of the Reynolds's result.

As main results, we will derive the continuity equation, the Cauchy stress tensor theorem, an evolution equation for the local behavior of the linear momentum and energy, and an inequality for the local entropy. As interface (boundary) conditions across the discontinuity surface $\Sigma(t)$ we obtain: $\llbracket \mathbb{T}\mathbf{n} \rrbracket = 0$ and $\llbracket \mathbf{q} \cdot \mathbf{n} \rrbracket = 0$. On top of this, using the conservation of the angular momentum one can also derive the symmetry of the stress tensor, i.e., $\mathbb{T}^T = \mathbb{T}$.

Theorem 2.1 (Reynolds Transport Theorem) *Let $\Omega'_R \subseteq \Omega_R$ be a bounded set and take $\Omega'(t) \subseteq \Omega(t)$, with $\Omega'(t)$ and $\Omega(t)$ the respective image of the sets Ω'_R and Ω_R through the C^2 diffeomorphism \mathcal{L}_t . Let $\varphi \in C^1((\bar{S} \times \bar{\Omega}(t)))$. Then*

$$\begin{aligned}
\frac{d}{dt} \int_{\Omega'(t)} \varphi(t, \mathbf{x}) dx &= \int_{\Omega'(t)} \left(\frac{D\varphi}{Dt} + \varphi \operatorname{div}(\mathbf{v}) \right) d\mathbf{x} \\
&= \int_{\Omega'(t)} \left(\frac{\partial \varphi}{\partial t} + \operatorname{div}(\varphi \mathbf{v}) \right) d\mathbf{x} \\
&= \int_{\Omega'(t)} \partial_t \varphi dx + \int_{\partial \Omega'(t)} \varphi \mathbf{v} \cdot \mathbf{n} d\sigma_x. \quad (2.10)
\end{aligned}$$

Proof (of Theorem 2.1) Denote by J_t the Jacobian of the transformation $\mathbf{x} = \mathcal{L}_t(\boldsymbol{\xi}, t) \in \Omega(t)$ for $\boldsymbol{\xi} \in \Omega_R$. Fix arbitrarily $\Omega'_R \subseteq \Omega_R$. We proceed as follows:

$$\begin{aligned}
\frac{d}{dt} \int_{\Omega'(t)} \varphi(t, \mathbf{x}) dx &= \frac{d}{dt} \int_{\Omega'(0)} \hat{\varphi}(t, \boldsymbol{\xi}) \hat{J}_t(\boldsymbol{\xi}) d\boldsymbol{\xi} \\
&= \int_{\Omega'_R} \frac{d}{dt} \left(\hat{\varphi}(t, \boldsymbol{\xi}) \hat{J}_t(\boldsymbol{\xi}) \right) d\boldsymbol{\xi} \\
&= \int_{\Omega'_R} \left(\frac{d\hat{\varphi}}{dt}(t, \boldsymbol{\xi}) \hat{J}_t(\boldsymbol{\xi}) + \hat{\varphi}(t, \boldsymbol{\xi}) \frac{\partial \hat{J}_t}{\partial t}(\boldsymbol{\xi}) d\boldsymbol{\xi} \right) \\
&= \int_{\Omega'(t)} \left(\frac{D\varphi}{Dt}(t, \mathbf{x}) + \varphi(t, \mathbf{x}) \operatorname{div}(\mathbf{v}(t, \mathbf{x})) \right) d\mathbf{x}. \quad (2.11)
\end{aligned}$$

This calculation concludes the proof of the Theorem.

See also Theorem 70.7 and Problem 70.1 in [Zei88].

2.3.1 The Continuity Equation

We recall that the mass of a body filling $\Omega(t)$ is given by

$$m(\Omega(t)) = \int_{\Omega(t)} d\mu_m = \int_{\Omega(t)} \rho d\mathbf{x}.$$

Taking $\varphi = \rho$ in Theorem 2.1 leads to

$$\frac{d}{dt} \left(\int_{\Omega'(t)} d\mu_m \right) = \int_{\Omega'(t)} [\partial_t \rho + \operatorname{div}(\rho \mathbf{v})] d\mathbf{x} = 0$$

for all $\Omega'(t) \subset \Omega(t)$. This means that

$$\partial_t \rho + \operatorname{div}(\rho \mathbf{v}) = 0 \text{ a.e. in } \Omega(t). \quad (2.12)$$

We refer to (2.12) as the continuity equation.

Note that if $\rho = \text{const.}$, then $\text{div}(\mathbf{v}) = 0$ (the *incompressibility constraint* holds), and hence, $\frac{d}{dt} J_t = 0$.

Choosing now $\varphi = 1$ in Theorem 2.1 gives

$$\frac{d}{dt} \left(\int_{\Omega'(t)} dx \right) = 0 \text{ for all } \Omega'(t) \subset \Omega(t).$$

This shows that the motion of an incompressible fluid conserves the volume, i.e., the motion is *isochoric*.

2.3.2 Derivation of the Momentum Equation

We would like to extend the Newton's law "*Force = mass \times acceleration*", which is typically valid for systems of (Newtonian) particles, to the case of a continuous medium. In order to do this, we need to shed some light on the concept of *force*. Here we distinguish between *body forces* and *contact forces*.

2.3.2.1 Body Forces

Body forces are those forces that can be assumed to be proportional to the mass of the body. This is somehow resembling the classical Newton's law, but note however that the choice of the body force is rather arbitrary. For convenience, we denote the specific body force by $\mathbf{f}^b : S \times \Omega(t) \rightarrow \mathbb{R}^3$, while the total body force exerted on $\Omega(t)$ is

$$\int_{\Omega(t)} \rho \mathbf{f}^b dx.$$

The typical example of body force is the gravity force $\mathbf{f}^b = -g\mathbf{e}_3$.

Other examples of body forces are, for instance, the attraction and repulsion forces posed at the continuum level, the steric interaction in colloidal systems, the electromagnetic force. They are often called *distance interactions*.

2.3.2.2 Contact Forces

The most intuitive example of a contact force is the *applied stress*, i.e., $\mathbf{t}^c : S \times \Gamma^{ext}(t) \rightarrow \mathbb{R}^3$. The quantity $\int_{\Gamma(t)} \mathbf{t}^c d\sigma$ describes the force felt by the surface $\Gamma(t)$.

The whole idea of the mechanics of a continuum relies on the existence of *internal (continuity, cohesion) forces*, say \mathbf{f}^i —these are forces that the continuum medium particles exert on each other and are responsible to maintain the continuity of the material during the motion. In most cases, it is difficult to identify the precise structure

of these forces. To address this matter, the **Cauchy Principle** postulates the existence of a vector field

$$\mathbf{t} : S \times \Omega(t) \times \{\mathbf{n} \in \mathbb{R}^3 : \|\mathbf{n}\| = 1\} \rightarrow \mathbb{R}^3$$

called *Cauchy stress*, such that

$$\int_{\partial\Omega'(t)} \mathbf{t}(t, \mathbf{x}, \mathbf{n}) d\sigma \quad (2.13)$$

is equivalent to the resultant of the material continuity (internal) forces acting on $\partial\Omega'(t)$. Here \mathbf{n} denotes the outward normal vector to $\partial\Omega'(t)$.

Note that

$$\mathbf{t} = \mathbf{t}^c \text{ on } \partial\Omega'(t).$$

Here \mathbf{t} depends on $\partial\Omega'(t)$ only through \mathbf{n} .

Cauchy's Principle relies on the following basic hypotheses:

- (H1) The contact force between two sub-bodies $\Omega_1(t)$ and $\Omega_2(t)$ in contact at the surface $\Gamma(t)$ can be represented by a vector measure $d\zeta$ concentrated on $\Gamma(t)$;
- (H2) the measure $d\zeta$ is absolutely continuous with respect to the measure $d\sigma$ such that

$$d\zeta = \mathbf{t}(\cdot) d\sigma,$$

where \mathbf{t} is the surface density of contact forces arising in (2.13).

2.3.2.3 Other Types of Forces

Most of the forces occurring in nonphysical systems [e.g. social systems, biology, finance] are not of “body” or “contact” nature. *Topological interactions*, governing for instance the motion of large swarms, are forces acting among a fixed number of particles. Their “continuum” counterpart is somewhat similar to Boltzmann-like *velocity interactions*. A similar role is played by *collisions*. The forces mentioned here play a role when for the discussed scenario the discrete and/or stochastic nature cannot be left out. Studying such inherently multiscale scenarios is mathematically interesting. Research in this direction is increasingly attracting the attention of the scientific community.

2.3.3 Principle of Conservation of Linear Momentum

For all $t \in S$ and all $\Omega'(t) \subset \Omega(t)$, we postulate

$$\frac{d}{dt} \int_{\Omega'(t)} \rho(t, \mathbf{x}) \mathbf{v}(t, \mathbf{x}) d\mathbf{x} = \int_{\Omega'(t)} \rho(t, \mathbf{x}) \mathbf{f}^b(t, \mathbf{x}) d\mathbf{x} + \int_{\partial\Omega'(t)} \mathbf{t}(t, \mathbf{x}, \mathbf{n}) d\sigma. \quad (2.14)$$

(2.14) is called the *principle of conservation of linear momentum*.

Theorem 2.2 (Law of action and reaction) *Let assume that for all $t \in S$ the functions \mathbf{f}^b , ρ , $\frac{D\mathbf{v}}{Dt}$ are bounded on $\Omega(t)$ and that \mathbf{t} is C^1 with respect to x and continuous with respect to \mathbf{n} . If for any sequence of subsets $\Omega'(t) \subset \Omega(t)$ we have*

$$\frac{1}{\sigma(\partial\Omega'(t))} \int_{\partial\Omega'(t)} \mathbf{t}(t, \mathbf{x}, \mathbf{n}) d\sigma \rightarrow 0 \text{ as } \lambda(\Omega'(t)) \rightarrow 0,$$

then

$$\mathbf{t}(t, \mathbf{x}, -\mathbf{n}) = -\mathbf{t}(t, \mathbf{x}, \mathbf{n}) \quad (2.15)$$

for all possible choices of \mathbf{n} with $\mathbf{x} \in \Omega(t)$

Proof See for instance [GS08], pp. 80–81.

Theorem 2.2 reflects a Newtonian principle that nicely fits physical systems. This does not necessarily hold in general. For instance, social systems are known not to respect it; see e.g. [Har10] (Fig. 2.1).

Theorem 2.3 (Cauchy's stress tensor theorem) *Let assume that for all $t \in S$ the functions \mathbf{f}^b , ρ , $\frac{D\mathbf{v}}{Dt}$ are bounded on $\Omega(t)$ and that \mathbf{t} is C^1 as a function of \mathbf{x} and continuous with respect to the normal \mathbf{n} . Then it exists*

$$\mathbb{T} : S \times \Omega(t) \rightarrow \mathbb{R}^{3 \times 3} \text{ such that } \mathbf{t}(t, \mathbf{x}, \mathbf{n}) = \mathbb{T}(t, \mathbf{x})\mathbf{n} \quad (2.16)$$

for all $t \in S$, all $\mathbf{x} \in \Omega(t)$, and all $\mathbf{n} \in \{\mathbf{n} \in \mathbb{R}^3 : \|\mathbf{n}\| = 1\}$.

Here \mathbb{T} is the so-called *Cauchy stress tensor*.

For a proof of Theorem 2.3, We refer the reader, for instance, to [TM05] (pp. 45–48).

So, $\mathbb{T}\mathbf{n} = \mathbf{t}$ a.e. on $\partial\Omega(t)$. So, the continuity (internal) forces can be seen as

$$\int_{\partial\Omega'} \tilde{\mathbf{t}}(t, \vec{\mathbf{x}}, \vec{\mathbf{n}}) dt = \int_{\partial\Omega'(t)} \mathbb{T}\mathbf{n} d\sigma \quad (2.17)$$

that is $\int_{\partial\Omega'(t)} \mathbb{T}\mathbf{n} d\sigma$ is the resultant of the internal forces. Based on (2.17), (2.14) becomes



Fig. 2.1 Flow of pedestrians close to Nakano station (Tokyo area), Japan, exhibiting non-Newtonian behavior close to corners. Note that the “fluid particles” do not cling on the walls. Interestingly, the “particles” seem to not like the corner at all

$$\frac{d}{dt} \int_{\Omega'(t)} \rho \mathbf{v} d\mathbf{x} = \int_{\Omega'(t)} \rho \mathbf{f}^b d\mathbf{x} + \int_{\partial\Omega'(t)} \mathbb{T} \mathbf{n} d\sigma. \quad (2.18)$$

Replacing $\varphi = \rho \vec{\sigma}$ in Theorem 2.1, from 2.11 and 2.12, we conclude that

$$\frac{d}{dt} \int_{\Omega'(t)} \rho \mathbf{v} d\mathbf{x} = \int_{\Omega'(t)} \rho \frac{D\mathbf{v}}{Dt} d\mathbf{x}. \quad (2.19)$$

Here $\frac{D\mathbf{v}}{Dt}$ is a sort of fluid acceleration term. Assuming $\text{div} \mathbb{T} \in L^1(\Omega(t))$, we get

$$\int_{\Omega'(t)} \left[\rho \frac{D\mathbf{v}}{Dt} - \text{div} \mathbb{T} - \rho \mathbf{f}^b \right] d\mathbf{x} = 0 \text{ for all } \Omega'(t) \subset \Omega(t). \quad (2.20)$$

This implies

$$\rho \frac{D\mathbf{v}}{Dt} - \text{div} \mathbb{T} - \rho \mathbf{f}^b = 0 \text{ a.e. in } \Omega(t). \quad (2.21)$$

Note that

$$\frac{D\mathbf{v}}{Dt} := \partial_t \mathbf{v} + (\mathbf{v} \cdot \nabla) \mathbf{v}, \quad (2.22)$$

where $(\mathbf{v} \cdot \nabla) \mathbf{v}$ is called convection term. With (2.22) in hand (2.21) becomes

$$\rho \partial_t \mathbf{v} + \rho (\mathbf{v} \cdot \nabla) \mathbf{v} - \operatorname{div} \mathbb{T} = \rho \mathbf{f}^b. \quad (2.23)$$

Note that (2.23) can be put into divergence form using the dyadic product of two vectors. This reads:

$$\rho \partial_t \mathbf{v} + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v} - \mathbb{T}) = \rho \mathbf{f}^b. \quad (2.24)$$

Recall that the dyadic product of any two vectors \mathbf{a} and \mathbf{b} is the second-order tensor

$$\mathbf{a} \otimes \mathbf{b} := \mathbf{a} \mathbf{b}^T := \begin{pmatrix} a_1 b_1 & a_1 b_2 & a_1 b_3 \\ a_2 b_1 & a_2 b_2 & a_2 b_3 \\ a_3 b_1 & a_3 b_2 & a_3 b_3 \end{pmatrix}.$$

In a static, or equilibrium state, the inertial term $\rho \frac{D\mathbf{v}}{Dt}$ in text and then (2.21) reduces to $\operatorname{div} \mathbb{T} + \rho \vec{f}^b = 0$, an equation which is essential in electrostatics.

2.3.4 Balance of the angular momentum

As the angular momentum is concerned, we postulate

$$\rho \left(\mathbf{x} \times \frac{D\mathbf{v}}{Dt} \right) = \rho (\mathbf{x} \times \mathbf{f}^b) + \operatorname{div}(\mathbf{x} \times \mathbb{T}). \quad (2.25)$$

More details can be found, for instance, in [vdV09], pp 49–51. Further remarks are given in Sect. 2.3.6.

2.3.5 Balance of Total Energy

Recall that for any $\Omega'(t) \subset \Omega(t)$, the kinetic energy at time $t \in S$ is

$$K(t) := \int_{\Omega'(t)} \frac{|\mathbf{v}|^2}{2} d\mu_m = \int_{\Omega'(t)} \frac{|\mathbf{v}|^2}{2} \rho dx, \quad (2.26)$$

the internal energy is

$$E(t) := \int_{\Omega'(t)} e d\mu_m = \int_{\Omega'(t)} e \rho dx, \quad (2.27)$$

while the entropy is given by

$$S(t) := \int_{\Omega'(t)} s d\mu_m = \int_{\Omega'(t)} s \rho dx. \quad (2.28)$$

Here $e = e(t, x)$ and $s = s(t, x)$ denote the internal energy density and entropy density, respectively.

Exercise 2.1 Derive a balance law for the kinetic energy directly from the balance of linear momentum. Do this by multiplying (2.21) by \mathbf{v} (see [Zei88], p. 442).

Following [Eva04], we have

$$\begin{aligned} \frac{d}{dt} \left(\int_{\Omega'(t)} \frac{\rho \mathbf{v}^2}{2} dx + \int_{\Omega'(t)} e \rho dx \right) &= \int_{\Omega'(t)} \mathbf{v} \cdot \mathbf{f}^b dx + \int_{\Omega'(t)} f_{Heat} dx \\ &+ \int_{\partial\Omega'(t)} \mathbf{v} \cdot \mathbb{T} \mathbf{n} d\sigma - \int_{\partial\Omega'(t)} \mathbf{q} \cdot \mathbf{n} d\sigma. \end{aligned} \quad (2.29)$$

Equation (2.29) means that the change of the total energy equals the rate of work performed (kinetic + internal) by the body $\Omega(t)$ and contact forces plus the body heat supply minus the heat flux escaping through $\partial\Omega'(t)$.

Relying also on the symmetry of the stress tensor \mathbb{T} , we obtain the local evolution laws:

$$\rho \frac{D}{Dt} \left(\frac{|\mathbf{v}|^2}{2} + e \right) = \rho \left(\mathbf{v} \cdot \mathbf{f}^b + f_{Heat} \right) + \operatorname{div}(\mathbb{T} \mathbf{v} - \mathbf{q}), \quad (2.30)$$

and

$$\rho \frac{De}{Dt} = \rho f_{Heat} - \operatorname{div}(\mathbf{q}) + \mathbb{T} : \mathbb{D}, \quad (2.31)$$

where

$$\mathbb{D} := \frac{1}{2} \left(\nabla \mathbf{v} + \nabla \mathbf{v}^T \right)$$

and

$$A : B := \sum_{i,j=1}^3 a_{ij} b_{ji}.$$

Remark 2.1 Replacing in (2.31) $e = c_v \theta$ leads to the classical heat conduction equation. The factor $c_v > 0$ is then the so-called specific heat.

Exercise 2.2 Formulate in your term the first law of thermodynamics.

Exercise 2.3 Propose a complete mathematical model able in principle to describe the balance of the total energy of the geometry Ω sketched in Fig. 2.2.

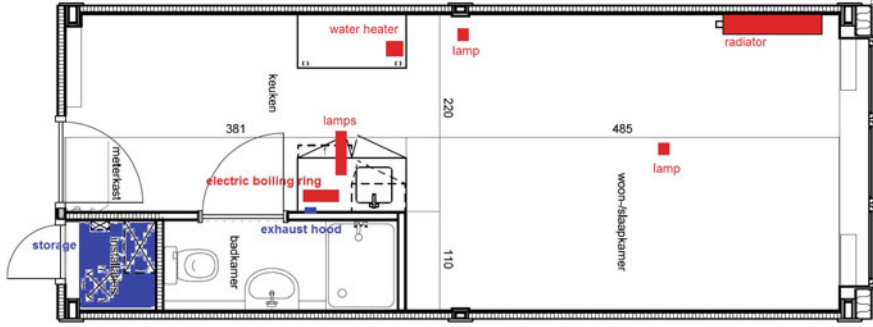


Fig. 2.2 How to ensure the thermal comfort in my flat?

2.3.6 Comments on Conservation of Momenta

Recall the definition of the *linear momentum*

$$\ell(\Omega'(t), t) := \int_{\Omega'(t)} \mathbf{v} \rho dx$$

and that of the *angular momentum*

$$\alpha(\Omega'(t), t) := \int_{\Omega'(t)} \mathbf{x} \times \mathbf{v} \rho dx.$$

Proposition 2.1 Show that for every part $\Omega'(t) \subset \Omega(t)$, we have

$$\frac{d}{dt} \ell(\Omega'(t), t) = \int_{\Omega'(t)} \rho \frac{D\mathbf{v}}{Dt} dx \quad (2.32)$$

$$\frac{d}{dt} \alpha(\Omega'(t), t) = \int_{\Omega'(t)} \mathbf{x} \times \rho \frac{D\mathbf{v}}{Dt} dx. \quad (2.33)$$

Proof We only indicate here as hint $\partial_t(\mathbf{x} \times \mathbf{v}) = \mathbf{x} \times \partial_t \mathbf{v} + \mathbf{v} \times \mathbf{v}$. But note also that $\mathbf{v} \times \mathbf{v} = 0$. For the details of the proof, see [Gur81], p. 92.

Definition 2.1 The center of mass, say $\mathbf{x}_c(t)$, at time t of the body $\Omega'(t)$ is defined as

$$\mathbf{x}_c(t) := \frac{1}{\mu_m(\Omega'(t))} \int_{\Omega'(t)} \mathbf{x} \rho dx. \quad (2.34)$$

Note that

$$\frac{d}{dt} \mathbf{x}_c(t) := \frac{1}{\mu_m(\Omega'(t))} \int_{\Omega'(t)} \mathbf{v} \rho d\mathbf{x}. \quad (2.35)$$

Corollary 2.1

$$\ell(\Omega'(t), t) = \mu_m(\Omega'(t)) \frac{d}{dt} \mathbf{x}_c(t). \quad (2.36)$$

It is worth noting that formula (2.36) gives a nice intuitive interpretation of the linear momentum. More precisely, “the linear momentum of a body $\Omega'(t)$ is the same as that of a particle of mass $\mu_m(\Omega'(t))$ attached to the center of mass of $\Omega'(t)$ ”, compare [Gur81], p. 93.

2.3.7 The Local Form of Clausius–Duhem Inequality, Admissible Thermodynamic Processes

In this section, we wish to give a criterium on which to rely when saying that our model (set of differential equations) complies with (continuum) thermodynamics. Here, we are narrowing down our attention to check whether the second principle of thermodynamics holds or not for the scenario in question. This is equivalent to verify whether the following inequality holds:

$$\frac{d}{dt} \left(\int_{\Omega'(t)} s d\mu_m \right) \geq \int_{\Omega'(t)} \frac{f_{Heat}}{\theta} d\mu_m - \int_{\partial\Omega'(t)} \frac{\mathbf{q} \cdot \mathbf{n}}{\theta} d\sigma. \quad (2.37)$$

We refer to (2.37) as the *Clausius–Duhem inequality*. This inequality means the following: The total entropy increase within $\Omega'(t)$ is greater or equal to the heat supply (by internal heat productions) over θ plus an entropy flux integrated over $\partial\Omega'(t)$. In other words, the entropy of system (open or close) can only increase.

The local variant of (2.37) is typically referred to as the *entropy inequality* and reads

$$\rho \frac{Ds}{Dt} \geq \frac{f_{Heat} \rho}{\theta} - \operatorname{div} \left(\frac{\mathbf{q}}{\theta} \right). \quad (2.38)$$

We define the *local production of entropy* per unit mass, say γ , to be

$$\begin{aligned} \gamma &:= \frac{Ds}{Dt} - \frac{f_{Heat}}{\theta} + \frac{1}{\rho} \operatorname{div} \left(\frac{\mathbf{q}}{\theta} \right) \\ &= \left[\frac{Ds}{Dt} - \frac{f_{Heat}}{\theta} + \frac{1}{\rho\theta} \operatorname{div}(\mathbf{q}) \right] - \frac{\mathbf{q} \cdot \nabla \theta}{\rho\theta^2}. \end{aligned} \quad (2.39)$$

Note that the entropy inequality (2.38) (which makes in (2.39) $[\dots] \geq 0$) together with the choice of the Fickian flux $\mathbf{q} = -K \nabla \theta$ (which keeps the term $-\frac{\mathbf{q} \cdot \nabla \theta}{\rho \theta^2}$ positive) lead to

$$\gamma \geq 0. \quad (2.40)$$

This is *the principle of positive (local) entropy production*. The proportionality factor K is the so-called *heat conduction coefficient*. This is a constant scalar for homogeneous and isotropic materials and a 2nd order tensor for nonhomogeneous (non-isotropic) materials. For porous materials, the heat conduction tensor reads

$$\mathbb{K} = \phi \tau K, \quad (2.41)$$

where ϕ is the porosity of the composite material (mixture of voids and fabric), the tensor τ is the tortuosity of the material (see [Bea88] for more on the tortuosity tensor¹), while K is the scalar heat conduction coefficient of the fabric material.

The quantity

$$\rho \theta \frac{Ds}{Dt} - \rho f_{Heat} + \operatorname{div}(\mathbf{q})$$

is typically referred to as the *internal density dissipation* field; see e.g. p.187 in [GS08].

Definition 2.2 We call a motion \mathcal{L}_t and a collection of functions (all unknowns, data and parameters) $\rho, \mathbf{v}, \mathbb{T}, f_{Heat}, \dots$ satisfying

- (a) the local conservation of mass
- (b) the local conservation of linear momentum
- (c) the local conservation of the angular momentum
- (d) the local conservation of total energy
- (e) the (global) Clausius-Duhem inequality

an *admissible thermodynamic process*.

Remark 2.2 For an admissible thermodynamic process to become an admissible solution to a certain mathematical model, further compatibility conditions need to be met. For instance, one hopes to know not only the needed constitutive laws for the stress tensor, but also the right transport fluxes and their behavior close to the boundary of the system (natural boundary conditions must be satisfied). Transport fluxes and other constitutive laws together with the issue of boundary conditions will be briefly discussed in the remaining part of this Chapter and in Chap. 3 (with a focus on transport fluxes).

¹Essentially, for composite materials made of simple microstructures the tortuosity tensor τ can be approximated.

It is the task of the applied mathematician to prove that the model is well-posed in the sense of Hadamard and herewith to ensure that the numerical solvability question of the model makes sense. Obviously, to ensure a certain quality and practical relevance of the well-posed model, the setting of the model equations must be validated against experimental data. Despite their crucial importance, well-posedness issues and the question of model validation are not discussed in these notes. Just as a hint, the reader may think in the direction of variational inequalities for treating the entropy inequality. For handling the other local formulations of the balance laws, suitable boundary conditions are needed. We discuss some of them in Sect. 2.4.

Exercise 2.4 Give a complete proof of Bernoulli's Theorem for (steady) conservative, irrotational flows.

Hint. Your starting point is the *Introduction to Continuum Mechanics* book by Gurtin, pp. 111–112. See also Proposition 2.2.

Exercise 2.5 Derive Torricelli's law.

Hint. See wikipedia. Basically, Torricelli states that the speed of efflux v of a fluid through a sharp-edged hole at the bottom of a tank filled to a depth h is the same as the speed that a body (in this case a drop of water) would acquire in falling freely from a height h , i.e., $v = \sqrt{2gh}$, where g is the acceleration due to gravity.

Exercise 2.6 In the Sect. 2.1 of the paper by K. Feigl, F.X. Tanner, B.J. Edwards, J.R. Collier, *A numerical study of the measurement of elongational viscosity of polymeric fluids in a semi-hyperbolically converging die*, J. Non-Newtonian Fluid Mech. 115 (2003) 191–215, there is an obvious mathematical error. Can you find it?

2.4 Towards Derivations of Boundary Conditions

2.4.1 Shocks

In this section, we want to account for the presence of discontinuities in the framework of the mechanics of continua. Part of the material presented here relies on [TM05], pp. 95–99.

When do discontinuities appear? For instance, they naturally show up when two materials are put in contact. However, there are many other types of discontinuities. Most interesting ones arise in jumps of the solution and their time and space derivatives (often called shocks). Although most of such discontinuities can be classified rigorously, we prefer to group them here as follows

- (A) Discontinuities in static quantities like in densities (e.g. at air-liquid interfaces), in \mathbb{T} (because of different constitutive laws), etc.
- (B) Discontinuities in kinematic quantities like in \mathbf{v} .

Let $\mathbf{x} = \mathcal{L}_t(\xi, t)$ if $\xi \in \Omega_R$ and $\mathbf{x} = \mathcal{S}_t(\zeta, t)$ if $\zeta \in \Sigma_R$ with $t \in S$, where Σ_R is a surface contained in the interior of Ω_R . If $\mathcal{L}_t|_{\Sigma_R} = \mathcal{S}_t$, then $\Sigma(t)$ moves with the

flow. However, in general we have no reasons to expect this to happen, especially if the surface $\Sigma(t)$ is an interesting one. For instance, the motion of such surface is triggered by an interface reaction (e.g. the corrosion of concrete with sulfuric acids), or it is precisely the place where a phase transition takes place (e.g. for the melting of ice scenario, $\Sigma(t)$ could be the boundary of the ice block, etc.). Therefore, in general, we expect $\mathcal{S}_t \neq \mathcal{L}_t|_{\Sigma_R}$, and hence, $\mathcal{L}_t^{-1}(\Sigma(t)) \neq \Sigma_R$.

We denote

$$\mathbf{v} := \frac{\partial \mathcal{L}_t}{\partial t}(\boldsymbol{\zeta}, t) \text{ “fluid” velocity} \quad (2.42)$$

$$\mathbf{w} := \frac{\partial \mathcal{S}_t}{\partial t}(\boldsymbol{\zeta}, t) \text{ velocity of the surface } \Sigma(t). \quad (2.43)$$

Generic assumption:

For any $t \in S$, we assume that $\Sigma(t)$ separates $\Omega(t)$ into two domains $\Omega_1(t)$ and $\Omega_2(t)$ and that

$$\mathcal{L}_t|_{\mathcal{L}^{-1}(\Omega_1(t))} \text{ and } \mathcal{L}_t|_{\mathcal{L}^{-1}(\Omega_2(t))}$$

are C^1 -mappings from $\mathcal{L}_t^{-1}(\Omega_i(t))$ into $\Omega_i(t)$ for $i \in \{1, 2\}$. Assume \mathcal{L}_t^{-1} to be a C^1 -mapping as well. Similar restrictions are needed for the mapping \mathcal{S}_t .

2.4.2 Rankine–Hugoniot Jump Relations

The aim of this section is to give a recipe to compute the quantity

$$\frac{d}{dt} \int_{\Omega(t)} \varphi(t, \mathbf{x}) d\mathbf{x},$$

where the function φ may have discontinuities across $\Sigma(t)$. A similar computation can be done for $\frac{d}{dt} \int_{\Sigma(t)} \psi(t, \mathbf{x}) d\sigma$. Note that the Reynolds Transport Theorem

$$\frac{d}{dt} \int_{\Omega(t)} \varphi d\mathbf{x} = \int_{\Omega(t)} \partial_t \varphi d\mathbf{x} + \int_{\partial\Omega(t)} \varphi \mathbf{v} \cdot \mathbf{n} d\sigma \quad (2.44)$$

applies to each $\Omega_i(t)$.

Proceeding this way, we obtain

$$\frac{d}{dt} \int_{\Omega_i(t)} \varphi d\mathbf{x} = \int_{\Omega_i(t)} \partial_t \varphi d\mathbf{x} + \int_{\partial\Omega_i(t) \cap \partial\Omega(t)} \varphi \mathbf{v} \cdot \mathbf{n} d\sigma + \int_{\Sigma(t)} \varphi \mathbf{w} \cdot \mathbf{n} d\sigma. \quad (2.45)$$

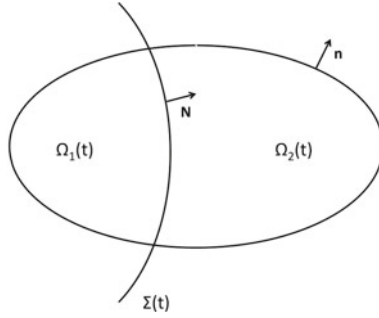


Fig. 2.3 Basic picture behind the derivation of Rankine–Hugoniot jump relations. $\Sigma(t)$ is a discontinuity surface separating the region $\Omega_1(t)$ from the region $\Omega_2(t)$

We interpret for the moment $\mathbf{v} = \mathbf{w}$ at $\Sigma(t)$. Note also that if \mathbf{N} denotes the normal to $\Sigma(t)$ from $\Omega_1(t)$ to $\Omega_2(t)$, then we have $\mathbf{n} = \mathbf{N}$ for $i = 1$ and $\mathbf{n} = -\mathbf{N}$ for $i = 2$; see Fig. 2.3.

Summing up now (2.45) for $i = 1$ and $i = 2$ leads to

$$\frac{d}{dt} \int_{\Omega(t)} \varphi d\mathbf{x} = \int_{\Omega(t)} \partial_t \varphi d\mathbf{x} + \int_{\partial\Omega(t)} \varphi \mathbf{v} \cdot \mathbf{n} d\sigma - \int_{\Sigma(t)} \llbracket \varphi \mathbf{w} \rrbracket \cdot \mathbf{N} d\sigma, \quad (2.46)$$

where $\llbracket Y \rrbracket := Y_2 - Y_1$ denotes the jump of Y through $\Sigma(t)$ for $Y_i := Y|_{\Omega_i(t)}$ ($i = 1, 2$).

Now, we rewrite (2.46) using the relative velocity

$$\mathbf{V} := \mathbf{v} - \mathbf{w}. \quad (2.47)$$

We obtain

$$\begin{aligned} \frac{d}{dt} \int_{\Omega(t)} \varphi d\mathbf{x} &= \int_{\Omega(t)} \partial_t \varphi d\mathbf{x} + \int_{\partial\Omega(t)} \varphi \mathbf{v} \cdot \mathbf{n} d\sigma - \int_{\Sigma(t)} [\varphi \mathbf{v}] \cdot \mathbf{n} d\sigma + \int_{\Sigma(t)} \llbracket \varphi \mathbf{V} \rrbracket \cdot \mathbf{n} d\sigma \\ &= \int_{\Omega_1(t) \cup \Omega_2(t)} [\partial_t \varphi + \operatorname{div}(\varphi \mathbf{v})] d\mathbf{x} + \int_{\Sigma(t)} \llbracket \varphi \mathbf{V} \rrbracket \cdot \mathbf{N} d\sigma. \end{aligned} \quad (2.48)$$

Note that for any function φ continuous across $\Sigma(t)$, we have $\llbracket \varphi \mathbf{V} \rrbracket_{\Sigma(t)} = 0$.

We assume that for each $\Omega'(t) \subset \Omega(t)$ the identity

$$\frac{d}{dt} \int_{\Omega'(t)} \varphi d\mathbf{x} = \int_{\Omega'(t)} f d\mathbf{x}$$

holds. Then the discussion in (2.48) shows that

$$\partial_t \varphi + \operatorname{div}(\varphi \mathbf{v}) = f \text{ a.e. in } \Omega_i(t) \quad i = 1, 2$$

and

$$[[\varphi \mathbf{v}]] \cdot \mathbf{N} = 0 \text{ a.e. on } \Sigma(t).$$

A nice derivation of the Rankine–Hugoniot conditions is given for instance in [Eva00], pp.137–140. It is worth noting at this stage that these conditions play a prominent role in selecting physically relevant solutions to conservation laws; compare [Daf00], e.g.,

Exercise 2.7 Take $\varphi := \rho v_i$ ($i \in \{1, 2, 3\}$) and derive the corresponding Rankine–Hugoniot (jump) relations at $\Sigma(t)$. Show that if *nothing happens* at $\Sigma(t)$, then $\mathbf{v} = 0$ and $[[\mathbf{T}\mathbf{N}]] = 0$.

A useful tool to derive boundary conditions is the so-called *shrinking pillbox principle* reported here in Lemma 2.1. For more details, see [Gur83], p. 28. Depending on the situation, we may interpret such limiting process also as a dimension reduction exercise; see [Chi02] for some ideas in this direction.

Lemma 2.1 (Pillbox Lemma) *For $t \in S$ with $t_0 \in S$ fixed such that $t > t_0$, let $\Omega_\varepsilon(t) \subseteq \Omega(t)$ be a pillbox with thickness $\varepsilon > 0$ supported on the flat interface $\Sigma(t_0)$ such that as $\varepsilon \rightarrow 0$ the pillbox $\Omega_\varepsilon(t)$ shrinks to $\Omega_0(t_0) := \Sigma(t_0) \subset \Omega(t)$. Let $\xi : \Omega_\varepsilon(t) \rightarrow \mathbb{R}$ and $\Xi : \Omega_\varepsilon(t) \rightarrow \mathbb{R}^3$ be two sufficiently smooth bulk fields. As $\varepsilon \rightarrow 0$, the following relations hold:*

$$\left\{ \frac{d}{dt} \int_{\Omega_\varepsilon(t)} \xi dx \right\}_{t=t_0} \rightarrow - \int_{\Sigma(t_0)} [[\xi]] \mathbf{V} d\sigma \quad (2.49)$$

$$\left\{ \frac{d}{dt} \int_{\partial\Omega_\varepsilon(t)} \Xi \cdot \mathbf{n}_\varepsilon d\sigma \right\}_{t=t_0} \rightarrow - \int_{\Sigma(t_0)} [[\Xi]] \cdot \mathbf{n} d\sigma, \quad (2.50)$$

where \mathbf{V} is cf. (2.47), \mathbf{n}_ε is the outer normal to $\partial\Omega_\varepsilon(t)$, while \mathbf{n} is the outer normal to $\Sigma(t_0)$.

2.4.3 Practical Examples of Boundary Conditions

2.4.3.1 The Case of the Navier–Stokes Equations

We wish to indicate here possible boundary conditions for the balance of the linear momentum applied to a viscous incompressible fluid; see (2.21). For simplicity, we consider now a fixed domain Ω such that $\partial\Omega := \Gamma^N \cup \Gamma^D$, where $\Gamma^D \cap \Gamma^N = \emptyset$ and $\sigma(\Gamma^D) \neq \emptyset$. We refer to Γ^N as the Neumann boundary and to Γ^D as the Dirichlet boundary.



Fig. 2.4 Place a water droplet on a solid surface. Drop on it dust of *pink* chalk. Wait a couple of minutes and you will see on the water droplet a boundary layer with a nearly constant width

The standard boundary conditions for an incompressible fluid are:

- *applied stress* (Neumann boundary condition)

$$\mathbb{T}\mathbf{n} = -p\mathbf{n} + 2\eta\mathbb{D}(\mathbf{v})\mathbf{n} = \mathbf{t}^c \text{ at } \Gamma^N$$

- *prescribed velocity* (Dirichlet boundary condition)

$$\mathbf{v} = \mathbf{g} \text{ at } \Gamma^D.$$

Often viscous fluids can be assumed to stick to walls, therefore the *no slip* boundary condition

$$\mathbf{v} = \mathbf{0}.$$

See further Sect. 2.5.1 (paragraph (iii)).

Remark 2.3 Even if one focusses on a single local balance law (say the balance of linear momentum), what are the right boundary conditions for an arbitrarily given scenario is an issue very difficult to address in full generality.

Let us take a simple example: Think for instance of two materials put in contact with each other. Let us make a straightforward experiment as illustrated in Fig. 2.4. On a drop of water lying on table drip small dust from a pink chalk. After 2 minutes of waiting, notice the occurrence of three possible different interfaces: (1) the water/table interface, (2) the white part of the top interface [between water and air] and (3) the dark pink part of the water–air interface. On each of these interfaces,

we expect that different boundary conditions apply. The most interesting part is (3)—a boundary layer where surfactant forces succeeded to collect nearly all chalk. If the boundary conditions on the parts (1) and (2) are a sort of clear, on the part (3) much debate is still ongoing. If one can assume the droplet to be stationary, then a Young–Laplace-type boundary condition could be possibly be applied. Note, however, that the thickness of this boundary layer is *a priori* unknown.

2.4.3.2 The Case of the Heat Conduction Equation: Possible Choices of Boundary Conditions

As discussed in Remark 2.3 about boundary conditions for momentum, also for heat conduction it is difficult to discuss what choices one has in general as boundary conditions. Usually, reasonable considerations can be made only if one fixes beforehand not only the class of balance equations² one has in mind, but also a physical experiment or a setup to which the envisaged boundary conditions should match.

Besides using standard Dirichlet boundary conditions (perfect contact with infinite heat reservoirs), homogeneous Neumann boundary conditions (perfect heat insulation), the dynamic boundary condition (2.87), and the Robin-like boundary condition (2.86), a few other boundary conditions can be used depending on the situation. A specific boundary condition is the Nernst radiation condition, i.e.,

$$-k \nabla \theta \cdot \mathbf{n} = \alpha(\theta - \theta_T)^4, \quad (2.51)$$

where θ_T is a constant translation value. If in (2.51) θ denotes the absolute temperature, then θ_T vanishes.

When two hot bodies (having temperatures θ_1 , and respectively, θ_2) come into a stationary contact (i.e., the contact surface is stationary) another prominent situation appears. Assuming the contact to be perfect along some surface $\Gamma := \Omega_1 \cap \Omega_2$, then transfer of heat across Γ can be described by means of *transmission boundary conditions*, viz. for all $t \in S$ and $x \in \Gamma$ we have

$$[\theta]_\Gamma = 0 \quad (2.52)$$

$$[-k(x) \nabla \theta \cdot \mathbf{n}]_\Gamma = 0. \quad (2.53)$$

Here the bracket $[\cdot]$ denotes $[\varphi]_\Gamma(x) := \varphi_2(x) - \varphi_1(x)$ for $x \in \Gamma$. Furthermore, we denoted

$$\theta(x, t) := \begin{cases} \theta_1(x, t), & \text{for } x \in \Omega_1 \\ \theta_2(x, t), & \text{for } x \in \Omega_2 \end{cases},$$

$$k(x) := \begin{cases} k_1, & \text{for } x \in \Omega_1 \\ k_2, & \text{for } x \in \Omega_2 \end{cases}.$$

²In particular, the order of the involved partial differential equations matters here.

If phase transitions are assumed to take place at the contact surface, then they can trigger the motion of the surface. This is, for instance, the case of the ice melting problem. Let us consider for a moment a water region, say $\Omega_1(t)$ surrounding an ice block denoted by $\Omega_2(t)$. Let $\Gamma(t)$ be the surface separating the ice and water regions. If θ_j denotes the temperature of $\Omega_j(t)$ ($j \in \{1, 2\}$), then the classical boundary conditions describing the melting of the ice in water are: for all $x \in \Gamma(t)$

$$\theta_1(x, t) = \theta_2(x, t) = \theta_{\text{melt}} \quad (2.54)$$

$$-k_2 \nabla \theta_2 \cdot \mathbf{n} + -k_1 \nabla \theta_1 \cdot \mathbf{n} = \mathfrak{L} V_n, \quad (2.55)$$

where \mathfrak{L} denotes the latent heat of the ice–water transition while V_n represents the normal component of the velocity of the moving interface $\Gamma(t)$. In (2.54), θ_{melt} denotes the melting temperature.

Exercise 2.8 Derive the moving boundary conditions (2.54) and (2.55).

The reader should not imagine that our list of boundary conditions for the heat equation is exhaustive. These choices are the most obvious ones, other ideas being still possible. Think for instance of a possible accumulation of heat at a boundary.

Exercise 2.9 How would you model heat accumulation at a fixed interface?

Hint. See also Exercise 2.13.

2.4.3.3 Modeling Mass Transfer at Gas-Liquid Interfaces

Instead of looking how two bodies exchange heat, let us consider for a moment how two bodies can exchange mass. We focus here the attention on the transfer of chemicals through water–air interfaces. For simplicity, let us consider an isothermal situation and try to describe the macroscopic transfer of a gaseous species $Y(g)$ into a water film. We denote by c_{Y_g} the concentration of $Y(g)$ and by c_{Y_w} the dissolved-in-water concentration $Y(aq)$. The equilibrium situation is described by *Raoult's law* which basically states that the partial pressure of $Y(g)$ equals the concentration of $Y(aq)$, viz.

$$p_{Y_g} = R c_{Y_w}, \quad (2.56)$$

where $R > 0$ is the Raoult's constant.

If one decides to model the situation only by means of reaction–diffusion systems,³ then it is convenient to use the translation of Raoult's law in terms of concentrations only, i.e.,

$$c_{Y_g} = H c_{Y_w}. \quad (2.57)$$

³A detailed modeling of the flow (and particularly of the pressure) is then avoided by deciding for simple fluid motions.

The expression (2.57) is the so-called *Henry's law*, where $H > 0$ is the Henry constant. If this is assumed to be truly a surface mechanism, then it typically enters a transmission condition at the air–water interface $\Gamma^{g/w}$. Usually, one imposes

$$[j \cdot n]_{\Gamma^{g/w}} = \pm \alpha (c_{Y_g} - H c_{Y_w}), \quad (2.58)$$

with α being an interfacial mass–transfer coefficient. Here $[j \cdot n]_{\Gamma^{g/w}}$ represents the flux of concentration Y passing through $\Gamma^{g/w}$. Note also that (2.57) points out a jump in the Y concentration while crossing $\Gamma^{g/w}$. In the same spirit as (2.58), one could also have

$$[j \cdot n]_{\Gamma^{g/w}} = \pm \beta (p_{Y_g} - R c_{Y_w}), \quad (2.59)$$

with $R > 0$ being the constant entering Raoult's law. Here $\beta > 0$ is the corresponding interfacial mass transfer coefficient.

Note that (2.58) describes how the mass transfer happens in the water and air phases, while (2.59) describes how mass is rearranged across the air–water interface. Interestingly, a similar structure as (2.58) can be used to model dissolution or precipitation from/to a water solid interface $\Gamma^{w/s}$ as well as adsorption-desorption isotherms (e.g., BET isotherms) of liquids in contact with porous thin layers; compare [Log01].

2.5 Examples of Constitutive Equations

To close the system of partial differential equations, we need to provide constitutive equations for the stress tensor \mathbb{T} and the transport flux \mathbf{j} of matter. The constitutive equations must be compatible with the principle of *admissible thermodynamic processes* and must be *objective* (i.e., frame indifferent).

2.5.1 Constitutive Equations for the Stress Tensor \mathbb{T}

Finding the right structure of the stress tensor is typically the task of *rheology*—branch of science trying to establish (macroscopic) connections between *stresses* and *kinematic* quantities.

- (i) *Elastic medium (general, nonlinear)*. A characteristic feature of an elastic body is that when it is deformed under some load, it returns to its undeformed reference state once the load is removed. In other words, in an elastic body, the momentary stresses (at time t) depend only on the momentary deformations (at time t), i.e.,

$$\mathbb{T} = \mathbb{T}(\mathbb{E}), \quad \mathbb{E} := \frac{1}{2} \left(\mathbb{F}^T \mathbb{F} - \mathbb{I} \right),$$

where \mathbb{E} is the Eulerian deformation tensor.

For a *linear elastic medium*, one benefits of the Hooke's law

$$\mathbb{T} = \lambda \text{tr}(\mathbb{E}) + 2\mu \mathbb{E},$$

where λ and μ are the Lamé coefficients and \mathbb{E} is here the linear deformation tensor with entries

$$e_{ij} := \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right),$$

while \mathbf{u} is the displacement vector.

- (ii) *Linear thermoelastic medium*. This is the case when one typically assumes the Hooke-Duhamel's law

$$e_{ij} = \frac{1}{2\mu} \left(t_{ij} - \frac{\lambda}{2\mu + 3\lambda} \delta_{ij} t_{kk} \right) + \alpha \Delta\theta,$$

where α is a linear expansion coefficient and $\Delta\theta$ is the temperature difference between the current temperature and a reference value. The total deformation is thus a linear superposition of elastic and thermal deformations.

- (iii) *Fluids*. The standard example is the *ideal fluid*, i.e.,

$$\mathbb{T} = -p\mathbb{I},$$

where the proportionality factor is called *pressure*. This is an example of non-viscous fluid.

A Newtonian incompressible fluid would satisfy

$$\mathbb{T} = -p\mathbb{I} + \eta \left(\nabla \mathbf{v} + \nabla \mathbf{v}^T \right).$$

This is an example of a viscous fluid. The parameter η is called *dynamic viscosity*.

The quantity

$$\mathbb{D}(\mathbf{v}) := \frac{1}{2} \left(\nabla \mathbf{v} + \nabla \mathbf{v}^T \right)$$

is called *strain-rate tensor*. Hence, we can rewrite \mathbb{T} as

$$\mathbb{T} = -p\mathbb{I} + 2\eta \mathbb{D}(\mathbf{v}). \tag{2.60}$$

For a Newtonian fluid, one assumes that η is independent of kinematic quantities [note that it might however depend on temperature]. Newtonian fluids are examples of *simple fluids*.

For *complex fluids*, we expect to have $\eta = \eta(\mathbb{D}(\mathbf{v}))$.

Remark 2.4 Combining (2.24) and (2.60) gives

$$\rho \partial_t \mathbf{v} + \rho (\mathbf{v} \cdot \nabla) \mathbf{v} + \nabla p - 2 \operatorname{div}(\eta \mathbb{D}(\mathbf{v})) = \rho \mathbf{f}^b. \quad (2.61)$$

Dividing (2.61) by ρ , denoting $P := \frac{p}{\rho}$ and assuming the kinematic viscosity $\nu := \frac{2\eta}{\rho}$ to be constant, then (2.61) becomes

$$\partial_t \mathbf{v} + (\mathbf{v} \cdot \nabla) \mathbf{v} + \nabla P - \nu \Delta \mathbf{v} = \mathbf{f}^b. \quad (2.62)$$

Equations (2.62) together with $\operatorname{div}(\mathbf{v}) = 0$ are called the Navier–Stokes equations for an incompressible fluid.

2.5.2 More on Constitutive Laws: Deviations from Modeling Incompressible Fluids

For *compressible fluids*, one needs one more *constitutive law*, namely

$$p = h(\rho, \theta). \quad (2.63)$$

For instance, the law of ideal gases is often used instead of (2.63). If the fluid is heated, then one needs an additional constitutive law for the specific heat

$$\hat{c}_\theta = g(\rho, \theta). \quad (2.64)$$

Here $h(\cdot)$ and $g(\cdot)$ are suitable expressions that need to be identified usually based on an especially designed experiment.

We define the dimensionless number

$$Re := \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{|\mathbf{v}_{av}| x_m}{\nu},$$

where x_m is a suitable length scale (e.g. traveled length by the fluid), $|\mathbf{v}_{av}|$ average speed of the fluid, and ν is the kinematic viscosity. Re is the so-called Reynolds number. For $Re \ll 1$ one gets the *Stokes approximation* (i.e., the *Stokes equations*), viz.

$$\partial_t \mathbf{v} + \nabla P - \nu \Delta \mathbf{v} = \mathbf{f}^b. \quad (2.65)$$

Note that for $Re \gg 1$, the flow becomes unstable and enters the turbulent regime [which delimitates the validity of the Navier–Stokes equations].

Remark 2.5 If one wants to get the elasticity equations, then one needs to choose $\mathbb{T} = \mathbb{T}(\mathbb{E})$. If one wants to obtain the viscoelasticity equations, then one has to choose $\mathbb{T} = \mathbb{T}(\mathbb{D}, \mathbb{F}_t)$. If, on the other hand, we think now of a thermal-viscoelastic fluid, then we expect $\mathbb{T} = \mathbb{T}(\mathbb{D}, \mathbb{E}, \theta, \nabla\theta)$, and so on.

2.5.3 Summary of Equations to Viscous and Inviscid Fluids

Following [Zei88], pp. 438–439, we list here the summary of equations for viscous and inviscid compressible fluids:

(i) the continuity equation

$$\rho_t + \operatorname{div}(\rho \mathbf{v}) = 0$$

(ii) the equation of motion (balance of linear momentum)

$$\rho \mathbf{v}_t + \rho(\mathbf{v} \nabla) \mathbf{v} - \mu \Delta \mathbf{v} = \rho \mathbf{f}^b - \nabla p.$$

(iii) the density–pressure relation

$$\rho = \rho(p).$$

It is important to be aware of a few particular situations. For instance, if $\rho = \text{const}$, then the fluid is called incompressible, and hence, (i) implies $\operatorname{div}(\mathbf{v}) = 0$. Another important particular scenario is when $\operatorname{curl}(\mathbf{v}) = 0$. This makes the flow *irrotational*.

Proposition 2.2 (Bernoulli’s law) *For a solution of equations (i)–(iii) in a connected flow region, the Bernoulli’s equation*

$$\frac{1}{2} |\mathbf{v}|^2 + U + \int_{p_0}^p \frac{dp}{\rho(p)} = \text{const}. \quad (2.66)$$

is valid if the flow is stationary and irrotational, and the body forces \mathbf{f}^b posses a potential (i.e., $\mathbf{f}^b = -\rho \nabla U$).

Note that a fluid is called *inviscid* if $\nu = 0$ (the inner friction is zero). Then the equations (i)–(iii) are called Euler equations. Inviscid fluids are also called *ideal fluids*.

2.5.4 How to Account for Temperature Effects on Fluids?

The question now is how to modify the basic fluid equations to account for temperature effects. This issue is related to the so-called *Bénard problem* [see also *Bénard–Rayleigh convection, instability, bifurcation*].

- (i) the continuity equation

$$\rho_t + \operatorname{div}(\rho \mathbf{v}) = 0$$

- (ii) the equation of motion (balance of linear momentum)

$$\rho \mathbf{v}_t + \rho(\mathbf{v} \nabla) \mathbf{v} + \nabla(-\mu \nabla \mathbf{v} + \tilde{c} \mathbf{v} \theta) = \rho \mathbf{f}^b - \nabla p, \quad \tilde{c} > 0,$$

- (iii) the density-pressure relation

$$\rho = \rho(p, \theta).$$

- (iv) the heat equation (or total energy balance)

$$(c_v \rho \theta)_t + \operatorname{div}(-K \nabla \theta + \mathbf{v} \nabla \theta) = 0$$

Concerning (iii), we note that one can take e.g. $\rho = \rho_0 - \alpha \rho_0(\theta - \theta_0)$, where $\alpha > 0$ and ρ_0 and θ_0 are constants. For instance, θ_0 can be a constant average temperature. Furthermore, one can also expect that the viscosity depends on temperature as well. Such a constitutive law is rather difficult to obtain.

Based on similarity arguments, one could think of

$$\eta(\theta) = c_\eta e^{-\iota \theta}, \quad (2.67)$$

with $c_\eta > 0$ and $\iota > 0$ suitable constants; see [Paw71], pp. 86–89. Other choices are also possible.

It is worth mentioning that a similar dependence as (2.67) can be used to couple the blood viscosity to the fibrin concentration transported by the blood to model the initiation of thrombosis. Finally, by using a concentration-dependent dynamic viscosity one aims at capturing the clot formation in the convected blood.

2.5.5 Summary of Equations for a Material (Fluid or Solid) Undergoing an Admissible Thermodynamics Process

Basic Equations

- (i) the continuity equation

$$\rho_t + \operatorname{div}(\rho \mathbf{v}) = 0$$

(ii) the equation of motion (balance of linear momentum)

$$(\rho \mathbf{v})_t + (\mathbf{v} \cdot \nabla)(\rho \mathbf{v}) - \operatorname{div} \mathbb{T} = \rho \mathbf{f}^b,$$

(iii) the balance of energy

$$(\rho e)_t + (\mathbf{v} \cdot \nabla)(\rho e) + \operatorname{div}(\mathbf{q}) = \rho f_{Heat} + \mathbb{T} : \mathbb{D},$$

(iv) Constitutive laws

$$e = c_v \theta \tag{2.68}$$

$$\rho = \rho(p, \theta). \tag{2.69}$$

$$\mathbb{T} = \mathbb{T}(p, \mathbb{F}_t, \mathbb{D}, \dots) \tag{2.70}$$

$$c_v = c_v(p, \theta); \tag{2.71}$$

(v) the entropy inequality

$$\partial_t(\rho s) + (\mathbf{v} \cdot \nabla)(\rho s) \geq \frac{f_{Heat} \rho}{\theta} - \operatorname{div} \left(\frac{\mathbf{q}}{\theta} \right).$$

Remark 2.6 (a) Choose for \mathbf{q} the Fourier law.

(b) Note also that (v) implies the Clausius-Duhem inequality.

(c) To complete a model based on partial differential equations, we need not only initial and boundary conditions but also typical values for all the model parameters.

Exercise 2.10 We consider a gas in a reactor that is modeled by the Frank-Kamenetskii's theory of heat explosion, i.e., the temperature θ satisfies for all $t \geq 0$ the equation

$$\partial_t \theta = \partial_{xx} \theta + \beta e^{Z\theta} \text{ where } x \in (0, L) \text{ with } \theta(0) = \partial_x \theta(L) = 0 \tag{2.72}$$

(i) Which sign would you expect for the parameters β and Z . Motivate your answer?

(ii) Consider the stationary case of (2.72). Which of the following statements is true?

(a) $\partial_x \theta = \sqrt{\beta} e^{\frac{Z\theta}{2}} \sqrt{\theta}$ a.e. in $(0, L)$.

(b) $\frac{1}{2} \beta |\partial_x \theta(0)|^2 = e^{Z\theta(L)} - 1$.

(iii) Give an analytical solution (or at least a reasonable approximation) to the stationary version of (2.72)?

(iv) Solve the stationary version of (2.72) numerically (in MATLAB). Compare your analytical and numerical approximations of the solutions.

Hint for (ii). Suggest a weak formulation and play games with it by choosing different suitable test functions.

2.6 Constitutive Equations for Transport Fluxes \mathbf{j} and \mathbf{q}

We list here a few examples of transport fluxes, such as

- *Molecular diffusion.*

$$\mathbf{j} := -D \nabla c \quad \text{Fick's law; } D \text{ diffusion coefficient, } c \text{ concentration;} \quad (2.73)$$

- *Advection-diffusion of chemicals.*

$$\mathbf{j} := -D \nabla c + \mathbf{v} c \quad \text{advection-diffusion; } D, c \text{ cf. (2.73), } \mathbf{v} \text{ flow velocity;} \quad (2.74)$$

- *Heat conduction.*

$$\mathbf{q} := -K \nabla \theta \quad \text{Fourier's law; } K \text{ heat conductivity, } \theta \text{ temperature;} \quad (2.75)$$

- *Flow through porous media.*

$$\mathbf{j} := -\mathbb{K} \nabla p \quad \text{Darcy's law; } \mathbb{K} \text{ permeability tensor, } p \text{ pressure;} \quad (2.76)$$

- *Cross-diffusion. Thermodiffusion.*

$$\mathbf{j} := -D_1 \nabla c_1 - D_2 \nabla c_2 \quad \text{Cross-diffusion;} \\ \text{Thermodiffusion for } (c_1, c_2) := (c, \theta), D_2 := K. \quad (2.77)$$

Remark 2.7 (i) We would like to draw the attention to

$$\mathbf{j} + \partial_t \mathbf{j} := -K \nabla \theta \quad (2.78)$$

the so-called *Cattaneo's law* for heat conduction, where K is the heat conductivity and θ temperature. By using the Cattaneo's choice of flux, the heat conduction equation becomes a telegraph-like equation.

(ii) It is worth noting that Darcy's law defines a purely macroscopic flux, while all the other fluxes enumerated above can be formulated at both macroscopic and microscopic level. In this course, if not specified otherwise, all quantities (including the fluxes) should be regarded as macroscopic objects.

(iii) In general, it is quite difficult to find the correct structure of the transport flux \mathbf{j} . Notorious difficulties arise either when multiple physics are involved like in thermodiffusion, plasma physics, galvano-mechanics and so on, or when living particles (ants, bacteria, humans, etc.) participate actively in the transport process.

See further Chap. 3 for a more detailed discussion of the derivation of the transport fluxes for the case of flow through a fully saturated porous medium and for the case of thermodiffusion.

2.7 Practical Examples

This section contains a collection of modeling exercises inspired by practical examples.

2.7.1 Model for a Simple Fluid—The Poiseuille Flow

Often in our modeling practice we may assume that we actually deal with simple fluids. By “simple”, we mean in this section that it is sometimes sufficient to use analytically prescribed velocity flow profiles instead of the momentum balance equations.

Following [TM05], pp. 138–139, we consider here such a “simple fluid” scenario. We focus our attention on a stationary 2D flow between two parallel fixed plates given by the equations $x_2 = \pm h$ ($h > 0$) without external forces. Assume a velocity profile with $\mathbf{v} = (v_1, v_2)$ such that $v_2 = 0$ and $v_1 = v_1(x_2)$ satisfying $\text{div}(\mathbf{v}) = 0$.

Recall (2.62) (i.e., the Navier–Stokes equations) and observe that a few terms in these equations drop out. What remains is

$$-\nu \partial_{x_2 x_2}^2 v_1 + \partial_{x_1} p = 0 \quad (2.79)$$

and

$$\partial_{x_2} p = 0.$$

The latter gives $p = p(x_1)$. Consequently, we have

$$\frac{dp}{dx_1}(x_1) = \nu \frac{d^2 v_1}{dx_2^2}(x_2) := \mathcal{C},$$

where $\mathcal{C} \in \mathbb{R}$ is the common value. Then we find that

$$\begin{aligned} p &= -\mathcal{C} x_1 \\ v_1 &= -\frac{\mathcal{C}}{2\nu} x_2^2 + \alpha x_2 + \beta, \end{aligned} \quad (2.80)$$

where $\alpha, \beta \in \mathbb{R}$. Using the *nonslip boundary conditions*, we can easily obtain that

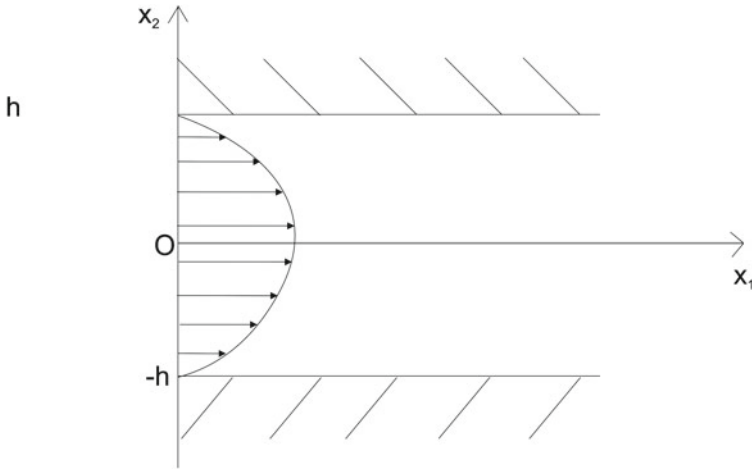


Fig. 2.5 The Poiseuille flow velocity profile

$$v_1(x_2) = \frac{\mathcal{C}}{2\nu} (h^2 - x_2^2). \quad (2.81)$$

Note v_1 given by (2.81) exhibits a parabolic profile.

If we assume that the upper plane $x_2 = h$ moves with constant velocity $V_0 \mathbf{e}_1$ and the lower plane is fixed (at $x_2 = 0$), then we get

$$v_1(x_2) = -\frac{\mathcal{C}}{2\nu} x_2(x_2 - h) + V_0 \frac{x_2}{h}.$$

Remark 2.8 With suitable boundary conditions at hand and for suitable geometries (e.g., tubes), one can still get explicit velocity profiles for the Poiseuille flow in 3D that are (still) parabolic (in the spirit of Fig. 2.5).

2.7.2 The Hot Coffee Problem

Let us consider now the following *Gedankenexperiment*: Imagine a cup filled with hot coffee on your working desk. The coffee is much too hot to be drunken immediately.

Exercise 2.11 Propose the simplest mathematical model able to estimate the time needed for the coffee temperature to reach a desired value, say θ_{des} .

One way to solve this exercise is the following:

To describe this situation, we select first the geometry of the cup. Let us restrict our attention to cups that have thermally isolated walls so that we can focus the

discussion on a one-dimensional cup (along the longitudinal direction). We denote it by $\hat{\Omega}$ filled with coffee until some level. Denote by $\Omega := (0, L) \subset \hat{\Omega}$ the part of the cup that is filled with coffee and let $x \in \Omega$ and $t \in S := (0, T_{fin})$ be our working variables. T_{fin} is here the final observation time of the coffee cup. The unknown is then the temperature $\theta(t, x)$. As data, we assume to know the initial temperature of the coffee θ_0 , the room temperature θ_R , as well as the values of the specific heat coefficient c_v for coffee as well as the heat conduction coefficient for coffee K . We observe that the modeling challenge is not really in deriving the evolution equation describing the evolution of the temperature in Ω , but rather in deriving the boundary conditions for the problem.

Assuming additionally that

(H1) the “evaporation” of heat takes place exclusively at the coffee–air interface $x = L$,

we propose the following model:

Find $\theta(t, x)$ satisfying

$$\partial_t(c_v\theta) + \partial_x(-K\partial_x\theta) = 0 \quad \text{a.e. in } S \times \Omega \quad (2.82)$$

together with the initial condition

$$u(0, x) = u_0 \text{ for all } x \in \bar{\Omega} \quad (2.83)$$

and the boundary conditions

$$-K \frac{\partial \theta}{\partial x}(t, 0) = 0 \quad (2.84)$$

$$-K \frac{\partial \theta}{\partial x}(t, L) = h(\theta)(\theta - \theta_R), \quad (2.85)$$

where $h : \mathbb{R}_+ \rightarrow \mathbb{R}_+$ is a transfer function defined by

$$h(s) := \begin{cases} \chi, & \text{if } s \geq \theta_R, \\ 0, & \text{if } s \leq \theta_R. \end{cases}$$

Here the parameter $\chi > 0$ is considered to be given. Note that the nonlinear Robin boundary condition (2.85) can be equivalently rewritten as

$$-K \frac{\partial \theta}{\partial x}(t, L) = \chi[\theta - \theta_R]^+,$$

where $[\cdot]^+$ denotes the positive part of a function. Recall that any given function f can be decomposed as $f = f^+ - f^-$, and $|f| = f^+ + f^-$, where $f^+ := \max\{f, 0\}$ and $f^- := \min\{f, 0\}$.

Remark 2.9 If one proves that for a.e. $(t, x) \in S \times \Omega$ one has $\theta_R \leq \theta(t, x) \leq \theta_0$, then (2.85) simply becomes the standard linear Robin boundary condition

$$-K \frac{\partial \theta}{\partial x}(t, L) = \chi(\theta - \theta_R). \quad (2.86)$$

Exercise 2.12 Imposing Dirichlet boundary conditions is often *unnatural*. Propose instead of (2.85) a Dirichlet boundary condition. Why is your choice actually incorrect from the modeling point of view?

Instead of (H1), assume now

(H2) the “evaporation” of heat takes place exclusively within a thin layer $[L - \varepsilon, L](\varepsilon > 0)$ adjacent to the coffee–air interface $x = L$.

Exercise 2.13 Assume (H2). Derive the *dynamic boundary condition*

$$\partial_t \theta(t, L) = h(\theta)(\theta - \theta_R). \quad (2.87)$$

Hint: Give suitable assumptions on the input data and then pass to the limit $\varepsilon \rightarrow 0$ in the equation

$$\partial_t(c_v \theta^\varepsilon) + \partial_x(-K \partial_x \theta^\varepsilon) = h(\theta^\varepsilon)(\theta^\varepsilon - \theta_R) \quad (2.88)$$

posed in the thin layer $S \times (L - \varepsilon, L)$. Use Lemma 2.1 with the choice $\xi := c_v \theta$.

2.7.3 Chemical Kinetics

In this section, we give a quick introduction to chemical kinetics. Essentially, this discussion is useful for writing the structure of the production terms (right-hand sides) in reaction–diffusion-type equations. It is worth noting that this is a useful modeling exercise not only for describing chemical engineering scenarios, but also to tackle situations from ecology, population dynamics, or phase transitions in composite materials (e.g. in steels).

For simplicity, we assume in this context that we are given a vessel, say Ω , containing $m \in \mathbb{N}$ reactants named here R_j ($j \in \{1, \dots, m\}$). Once the reactants R_j meet, they react together and, depending on the precise chemical mechanism, they turn into products, say P_k ($k \in \{1, \dots, M\}$). Concerning the reaction domain Ω , we assume that

- the *well-stirred reactor hypothesis* holds;
- the system in question is closed, completely isolated from its ambient.

Consequently, the balance equations describe what happens with the mass (or with the concentration) of the involved chemical species become ordinary differential equations.

Productions by Reactions, Reaction Rates

We consider the following prototypical reaction mechanism:

$$\sum_{j=1}^m r_j R_j \xrightarrow{k} \sum_{k=1}^M p_k P_k, \quad (2.89)$$

where

$$\begin{aligned} R_j &:= \text{reactants} \\ P_\ell &:= \text{products} \\ r_j, p_\ell &:= \text{stoichiometric coefficients} \\ k &:= \text{reaction constant.} \end{aligned}$$

We can reformulate (2.89) as follows:

$$\sum_{i=1}^{m+M} v_i Y_i \xrightarrow{k} 0, \quad (2.90)$$

where

$$v_i := \begin{cases} r_i, & i \in \{1, \dots, m\} \\ -p_i, & i \in \{m+1, \dots, m+M\} \end{cases} \quad (2.91)$$

Here

$$Y := (Y_1, Y_2, \dots, Y_{m+M}) = (R_1, R_2, \dots, R_m, P_1, P_2, \dots, P_M) \quad (2.92)$$

is the concentration vector. The vector of concentrations Y includes all chemically active species (both reactants and products).

The tacit assumption here is that $r_i \geq 0$, $p_\ell \geq 0$ for any $i \in \{1, \dots, m\}$ and $\ell \in \{m+1, \dots, M\}$, and also, that it exists at least an index i^* such that $v_{i^*} \neq 0$.

Note that for a general chemical reaction this question turns to be hard to answer; see [AsP02], e.g., However, for a special class of chemical reactions called elementary (simple) reactions, the answer to the above question turns to be very simple. This is the subject of the next paragraph.

Elementary Chemical Reactions

What do we actually know for sure? For chemical reactions (in the absence of transport), we can sometimes rely on the *total conversion assumption*: Essentially, *reactants* turn completely into *products*. It is worth noting that this assumption makes only sense if the chemicals receive sufficient time to react.

Definition 2.3 The quantity η_{R_j} defined by

$$\eta_{R_j} := r_j f_{P R_j}$$

is called *reaction rate*. Here r_j is the corresponding stoichiometric coefficient, while f_{PR_j} is the production rate by reaction corresponding to the reactant species R_j .

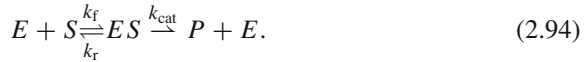
Note that the existence of f_{PR_j} can be mathematically guaranteed by a suitable application of the Radon–Nikodym theorem. However, the latter result does not construct f_{PR_j} , so we need to bring in the discussion further structural assumptions.

Definition 2.4 (*Elementary chemical reactions*) The reaction (2.89) is said to be elementary if and only if it exists $k > 0$ such that

$$\eta_{R_j} = k \prod_{j=1}^m c_{R_j}^{r_j}, \quad (2.93)$$

where c_{R_j} denotes the molar concentration of species R_j .

Let us now discuss the kinetics of a particular enzymatic reaction mechanism, the so-called *Michaelis–Menten* reaction. This reads



The mechanism (2.94) involves an enzyme E binding to a substrate S to form a complex ES that finally converts into a product P releasing back the enzyme E . We have selected this mechanism not only because it is a prominent one in the field of enzyme reactions, but also because it is actually a motive that can be used in situations away from chemistry, for instance, in population dynamics.

Let c_E , c_S , c_{ES} , and c_P be the corresponding molar concentrations involved in (2.94). Assuming a well-stirred situation, we write down the molar (mass) balance equations as follows:

$$\begin{aligned} \frac{dc_S}{dt} &= -k_f c_E c_S + k_r c_{ES} \\ \frac{dc_E}{dt} &= -k_f c_E c_S + k_r c_{ES} + k_{\text{cat}} c_{ES} \\ \frac{dc_{ES}}{dt} &= +k_f c_E c_S - k_r c_{ES} - k_{\text{cat}} c_{ES} \\ \frac{dc_P}{dt} &= +k_{\text{cat}} c_{ES}. \end{aligned} \quad (2.95)$$

To complete the system (2.95), we assign the initial conditions

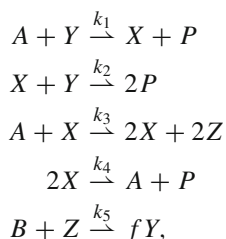
$$c_S(t=0) = c_{S0}, \quad c_E(t=0) = c_{E0}, \quad c_{ES}(t=0) = c_{ES0}, \quad c_P(t=0) = 0, \quad (2.96)$$

where c_{S0} , c_{E0} , $c_{ES0} \in \mathbb{R}_+$ are given. Note that, for instance, we have the combined reaction rate for the production of the enzyme E

$$\eta_E = r^* f_{PE} := -k_f c_E c_S + k_r c_{ES} + k_{\text{cat}} c_{ES},$$

where the stoichiometric coefficient is $r^* = 1$.

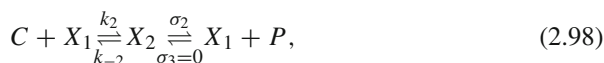
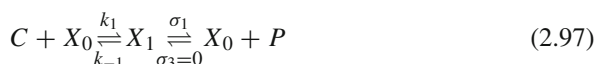
Exercise 2.14 Assume a vessel filled with a well-stirred liquid containing the chemical species A, B, X, Y, Z, P which undergo the *Oregonator* reaction mechanism (model for a certain class of autocatalytic reactions), i.e.,



where $f \in \mathbb{N}$ is a stoichiometric coefficient, while $k_i \in \mathbb{R}$ ($i \in \{1, \dots, 5\}$) are the corresponding reaction constants.

Write down the mass balance equations for all species.

Exercise 2.15 Consider the following chemical (cooperative) reaction mechanism:



where C, X_0, X_1, X_2 , and P are chemical species and k_ℓ ($\ell \in \{-2, -1, 1, 2\}$) and σ_j ($j \in \{1, 2, 3\}$) are reaction constants. Denote by c, x_0, x_1, x_2 , and p the molar concentrations of the chemical species C, X_0, X_1, X_2 , and P , respectively.

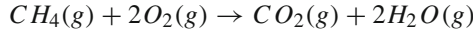
- Write down the mass balance equations corresponding to the mechanism (2.97)–(2.98).
- Identify at least one conserved quantity (i.e., a concentration or a linear combination of concentrations).
- Nondimensionalize the balance equations. Have you succeeded to obtain the same number of dimensionless parameters as predicted by Buckingham- Π theorem?

Exercise 2.16 Explain the connections between the Raoult's law and Henry's law (both describing the motion of molecules crossing a water–air interface). Motivate your answer.

Hint. See any good textbook on physical chemistry, for instance, compare [AdP02].

Exercise 2.17 Combustion is the sequence of exothermic chemical reactions between a fuel and an oxidant accompanied by the production of heat and conversion of chemical species. The release of heat can produce light in the form of either glowing

or a flame. In a complete combustion reaction, a compound (say methane) reacts with an oxidizing element, such as oxygen, and the products are compounds of each element in the fuel with the oxidizing element. In this case, the exothermic chemical reaction



releases (at room temperature and normal atmospheric pressure) 802 kJ/mol. Write down a complete system of balance equations describing the evolution of the four reacting gases in a combustion chamber, say $\Omega \subset \mathbb{R}^3$.

Hint. To be able to tackle this problem, you really need to fix a set of assumptions under which you want to work. Start with describing the geometry. Note that “size matters”.

2.7.4 Geothermal Flow

In this section, we give an example when multiphysics must be taken into account. In particular, the modeling of the heat transfer cannot be done decoupled from what happens with the fluid and solid mechanics of the situation.

Intelligent harvesting of geothermal energy must rely on a good understanding of heat and flow transport in heterogeneous media and eventual implications on soil mechanics. For instance, in the harvesting by open loop wells, the energy is retrieved from subsurface wells to provide heat to households. As the fluid moves from the aquifer through the piping, thermal energy is lost to the surrounding soil interplaying with the neighboring fluid and solid fabric. We refer the reader to [BOB14] and references cited therein for more details on this topic. We wish to build here a possible model to describe this particular geothermal scenario.

Let \mathbf{x} be a point in a macroscopic domain $\Omega \subset \mathbb{R}^3$ surrounding the well (borehole), and consider a typical pore $Y_{\mathbf{x}} \subset \mathbb{R}^3$ positioned at \mathbf{x} . Aquifers are by definition saturated with water. This fact allows us to model $Y_{\mathbf{x}}$ as composed of a (connected and simply connected) solid part $B_{\mathbf{x}}^1$ and a fluid part $B_{\mathbf{x}}^2$. Mathematically, $Y_{\mathbf{x}} = B_{\mathbf{x}}^1 \cup B_{\mathbf{x}}^2$, with the two (closed) domains intersecting along the boundary $\Gamma_{\mathbf{x}} = B_{\mathbf{x}}^1 \cap B_{\mathbf{x}}^2$. Our state variables in $Y_{\mathbf{x}}$ are a vector field of elastic displacements $\mathbf{U} : Y_{\mathbf{x}} \rightarrow \mathbb{R}^3$, temperature $\theta : Y_{\mathbf{x}} \rightarrow \mathbb{R}$ and flow velocity $\mathbf{v} : Y_{\mathbf{x}} \rightarrow \mathbb{R}^3$. We model their evolution by coupling linear thermoelasticity theory with Navier–Stokes flow, and hence start off from the following set of equations:

In the solid part $B_{\mathbf{x}}^1$, the unknowns $(U, \theta^s, \mathbb{T}^s)$ satisfy

$$\begin{aligned} \rho_r^s \partial_{tt} \mathbf{U} - \operatorname{div}(\mathbb{T}^s) &= \rho_r^s \mathbf{b}^s \\ \partial_t(\rho_r^s c_v^s \theta^s) + \operatorname{div}(\rho_r^s c_v^s \theta^s \partial_t \mathbf{U}) + \operatorname{div}(-D_s \nabla \theta^s) &= \operatorname{div}(\mathbb{D}^s \mathbb{T}^s) + \rho_r^s r^s \\ \mathbb{T}^s &= \mathbb{T}_{Hooke}(\mathbb{E}) + \gamma^s (\theta^s - \theta_r^s) \mathbb{I}. \end{aligned} \quad (2.99)$$

In the liquid part B_x^2 , the unknowns $(\rho^f, p, v, \theta^f, \mathbb{T}^f)$ satisfy

$$\begin{aligned}
 \partial_t \rho^f + \operatorname{div}(\rho^f \mathbf{v}) &= 0 \\
 \frac{\rho^f - \rho_r^f}{\rho_r^f} &= -\alpha(\theta^f - \theta_r^f) + \kappa(p - p_r) \\
 \partial_t(\rho^f \mathbf{v}) + (\mathbf{v} \nabla) \cdot (\rho^f \mathbf{v}) &= \operatorname{div} \mathbb{T}^f + \rho^f \mathbf{b}^f \\
 \partial_t(\rho^f c_v^f \theta^f) + \operatorname{div}(\rho^f c_v^f \theta^f \mathbf{v}) + \operatorname{div}(-D_f \nabla \theta^f) &= \operatorname{div}(\mathbb{D}^f \mathbb{T}^f) + \rho^f r^f \\
 \mathbb{T}^f &= -p \mathbb{I} + \eta \mathbb{D}^f. \quad (2.100)
 \end{aligned}$$

Here, \mathbf{b}^s and \mathbf{b}^f are body forces (e.g., gravity), r^s and r^f are heat sources, ρ_r^s and ρ_r^f are constant reference densities, η and ν are, respectively, dynamic and kinematic viscosities, while c_v^s , c_v^f and D_s , D_f are specific heat capacities and, respectively, diffusivities. Furthermore, α and γ^s are thermal expansion coefficients and κ is the compressibility parameter and θ_r^s and θ_r^f are constant reference temperatures.

$\mathbb{E}(\mathbf{U})$ is the strain tensor defined by

$$(\mathbb{E}(\mathbf{U}))_{i,j} = \frac{1}{2} \left(\frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i} \right).$$

The elasticity coefficients A entering Hooke's law $\mathbb{T}_{Hooke}(\mathbb{E}) = A(\cdots)\mathbb{E}(U)$ are given in terms of the Lamé coefficients λ and μ and the stress tensor,

$$\sigma_{Hooke}(U) = \lambda(\nabla \cdot \mathbf{U})\mathbb{I} + 2\mu\mathbb{E}(\mathbf{U}).$$

The term $\operatorname{tr}(\mathbb{T}^s : \mathbb{D}^s)$ is the so-called *dissipation heat*, while the rate of the deformation tensor \mathbb{D}^ℓ is defined as $\mathbb{D}^\ell = \partial_t \mathbb{E}^\ell$, $\ell \in \{s, f\}$.

As boundary conditions at Γ_x (material interface between B_x^1 and B_x^2), we take

$$\begin{aligned}
 \partial_t \mathbf{U} - \mathbf{v} &= 0 \\
 \mathbb{T}^s \mathbf{n}(\mathbf{x}) &= \mathbb{T}^f \mathbf{n}(\mathbf{x}) \\
 -D_s \nabla \theta^s \cdot \mathbf{n}(\mathbf{x}) &= -D_f \nabla \theta^f \cdot \mathbf{n}(\mathbf{x}) = m(\theta^f - \theta^s),
 \end{aligned}$$

where $\mathbf{n}(\mathbf{x})$ denotes the outer normal to Γ_x .

It is worth noting that m arising in the heat flux boundary conditions has a dual interpretation: m can be seen as a proportionality constant, or as a nonlinear function of the difference $\theta^f - \theta^s$.

Note that this scenario can be in principle extended further not only to include an eventual production of thermal fractures but also to incorporate phase transitions occurring due thermally activated chemical reactions in soils.

Some aquifers contain high salts concentration. In this case, both the elasticity coefficients A , λ , μ and the compressibility parameter κ may depend on the adsorbed concentration of salts. A possible functional choice is $A(\mathcal{F}(s))$, where $\mathcal{F}(s)$ is a

functional of the salt concentration s defined as

$$\mathcal{F}(s) := \int_0^t K(t - \tau) F(s) d\tau$$

with $K(t - \cdot)$ convolution kernel and $F(\cdot)$ nonlinear reaction rate. Correspondingly, the model equations have to be then extended to include the diffusion, advection, ionic decomposition (Nernst-Planck system) of the salts.

Exercise 2.18 Reformulate the geothermal flow equations (2.99) and (2.100) such that high salt concentrations are allowed to affect the flow and the mechanics of the situation.

2.8 Notes and Comments

Balance equations in continuum physics are explained in a huge number of textbooks and review papers. For a presentation from a mathematical perspective, our reference book is [Zei88]. For more on conservation laws, we recommend the monograph by C. Dafermos [Daf00]. An accessible survey of entropy methods for partial differential equations is given in [Eva04]. For intimate links between parabolic equations and thermodynamics, see [Day92]. An easy to read introduction to continuum thermodynamics is [Eva10].

Derivations of the Stefan's free boundary condition driving ice–water interfaces are given in many references; we refer the reader particularly to the nice derivation given in the lecture notes [And04]. Note that these conditions apply also in other contexts than the ice–water system. For instance, compare [MBK11, AM09] for a scenario involving moving sharp reaction fronts in concrete (the so-called concrete carbonation process). A nice mathematically rigorous derivation of Robin-like boundary conditions, very much in the spirit of the Pillbox Lemma (see Lemma 2.1), has been done in [AJCRB08].

Continuum Modeling

An Approach Through Practical Examples

Muntean, A.

2015, XIV, 73 p. 7 illus., 5 illus. in color., Softcover

ISBN: 978-3-319-22131-1