

Chapter 3

Continuum Thermodynamics of Single Fluid

In this chapter, we advance our exposition of rational thermodynamics further. The uniformity is abandoned and the description of space effects enters the scene. To keep the explanation simple, we deal with the rational thermodynamics of a single (pure) substance only (i.e., a substance composed of only one constituent as opposed to many constituent substances—mixtures—discussed in the following Chap. 4) and confine our discussion to fluids. We thus study properties changing not only in time but also in the space, but in such a way that the discrete structure of matter may be ignored. That is, we use the methods of continuum (thermo)mechanics by reducing properly the space scale (in comparison with uniform bodies of Chap. 2). On the other hand, the timescale will be similar to that in Chap. 2, i.e., we confine ourselves only to materials with differential memory. Finally, we discuss the linearized case, which is the most important model in applications, in the subsequent chapters of this book.¹

3.1 Kinematics of Continua

First, we review some basic concepts from deformation theory; although they are not needed in most applications for fluids they are necessary to develop and understand the general theory [6–13].

We study the *body* (composed of a single substance) and its *parts* which we perceive through their *configurations* (connected region in three-dimensional Euclidean space), which this body (or its parts) occupies or may occupy in the space.

¹ For simplicity we do not discuss bodies in which there exist surfaces of discontinuity even though such models are very important in chemical engineering, e.g., they model phase boundaries, surface chemical reactions, or shock waves. But even in such simplified models (ignoring specific surface phenomena like surface tension) [1, 2], we obtain the important results of phase equilibria (like equality of chemical potentials in bulk phases, cf. Sect. 2.5, which may be generalized to Eshelby tensors of chemical potentials, cf. Rem. 38, [2, 3]). Further generalization with surface phenomena uses *configurational forces* (in fluids these are chemical potentials related to unit volume) see [4, 5].

We select one arbitrary configuration as a *reference configuration* (we denote it simply as a “reference”) and radius vectors of points in such reference, \mathbf{X} , we call the *particles* of the body (identified with their positions).²

The motion of the body is described mathematically as the time succession of the *actual* configurations in real space. Namely, vector \mathbf{x} (relative to *frame* discussed in Sect. 3.2) gives the position of particle, \mathbf{X} , in the instant t through the vector function $\underline{\chi}$ called the *motion* or *deformation function* as

$$\mathbf{x} = \underline{\chi}(\mathbf{X}, t), \quad x^i = \chi^i(X^J, t) \quad i, J = 1, 2, 3 \quad (3.1)$$

The second expression is given in the component form (which is a concise form of $x^i = \chi^i(X^1, X^2, X^3, t)$). For simplicity, we use for the reference and actual configurations Cartesian coordinates only which need not coincide; therefore, we denote referential or actual (spatial) components by great or small upper Latin indices respectively. Motion (3.1) therefore assigns to every particle \mathbf{X} its place \mathbf{x} in the actual configuration in the instant t . A given body or its part contains in all its actual configurations the same particles (as in reference). For a given particle, the \mathbf{X} gives (3.1) its trajectory. A simple example of (3.1) is the rigid motion in Rem. 5, others (shear, volume expansion, etc.) may be easily written [9, 12, 14]. For simplicity, we assume that function (3.1) is smooth (continuous and differentiable in both variables) and invertible for \mathbf{X}

$$\mathbf{X} = \underline{\chi}^{-1}(\mathbf{x}, t) \quad (3.2)$$

Therefore, two particles cannot be present at the same place and conversely; we exclude from description such phenomena as a tearing or a penetrating of the bodies, destruction and origin of new particles and trajectories, crossing trajectories, etc. A typical quantity ψ we are interested in (which may be scalar, vector, or tensor) is a field, i.e.,

$$\psi = \psi(\mathbf{x}, t) \quad (3.3)$$

$$\psi = \psi(\mathbf{X}, t) \quad (3.4)$$

which are connected through (3.1) and (3.2). Using (3.3) we speak about *space* or *actual* (or *Euler*) description and using (3.4) we speak about *material* or *referential*,

² From a molecular point of view such a “macroscopic” particle \mathbf{X} contains a great number of molecules.

We fix this reference once and for all, but in the general theory the change in this reference may be used to describe the symmetry inherent to the material of the body; in the special case it may be used for the definition of fluid (cf. Sect. 3.5 and Rem. 30).

In some continuum theories of more complicated models (e.g., micromorphic or microcontinuous) \mathbf{X} may have some inner structure (cf. Rem. 26).

(or *Lagrange*) description of the field for quantity ψ . The time or space derivative in space description (3.3) we denote $\partial\psi/\partial t$ or $\text{grad}\psi$ (in components $\partial\psi/\partial x^i$), respectively, the time derivative in referential description (3.4) we denote by a dot

$$\dot{\psi} = \frac{\partial\psi(\mathbf{X}, t)}{\partial t} \quad (3.5)$$

and call it the *material* or *substantial* (time) derivative. This quantity expresses the change of ψ in time along the trajectory of the chosen particle. Gradient in the referential description we denote as Grad :

$$\text{Grad}\psi = \frac{\partial\psi(\mathbf{X}, t)}{\partial\mathbf{X}} \quad (3.6)$$

We define the *velocity* \mathbf{v} of a particle as the time (material) derivative of the motion (3.1)

$$\mathbf{v} \equiv \partial\underline{\chi}/\partial\mathbf{t} = \dot{\underline{\chi}} \quad (3.7)$$

From (3.1), (3.3), (3.5), and (3.7), it follows for material derivative

$$\dot{\psi} = \frac{\partial\psi}{\partial t} + v^i \frac{\partial\psi}{\partial x^i} = \frac{\partial\psi}{\partial t} + \mathbf{v} \cdot \text{grad}\psi \quad (3.8)$$

where the second expression is valid for scalar ψ (dot in r.h.s. denotes the scalar product); for vector ψ^j

$$\dot{\psi}^j = \frac{\partial\psi^j}{\partial t} + v^i \frac{\partial\psi^j}{\partial x^i} \quad (3.9)$$

Here we use the *summation rule*: we sum through the repeating indexes, e.g.,

$$v^i \frac{\partial\psi^j}{\partial x^i} = \sum_{i=1}^3 v^i \frac{\partial\psi^j}{\partial x^i}$$

Deformation gradient \mathbf{F} is a derivative of a motion $\underline{\chi}$ with respect to \mathbf{X}

$$\mathbf{F} = \frac{\partial\underline{\chi}}{\partial\mathbf{X}}, \quad F^{iJ} = \frac{\partial\chi^i}{\partial X^J} \quad (3.10)$$

It is a tensor of the second order³ which describes changes in the mutual position of two close particles during the change of configuration from reference to actual one as it is seen from

³ Defined in the following Rem. 4 generalized here in a (generally) different Cartesian system (here, a space and referential one). Then, e.g., the matrix of $\mathbf{F} = \mathbf{1}$ need not be the unit one (Kronecker delta), but a so-called shifter; cf. e.g. [9, 15]. Here, for simplicity, both Cartesian systems are mostly chosen as the same.

$$d\mathbf{x} = \mathbf{F} d\mathbf{X} \quad (3.11)$$

Because of the invertibility of motion

$$J \equiv |\det \mathbf{F}| > 0 \quad (3.12)$$

and inverse of \mathbf{F} , denoted by \mathbf{F}^{-1} (in components $F^{-1 Ji}$ is a gradient of χ^{-1} (3.2)). We note that

$$\text{Grad} \psi = (\text{grad} \psi) \mathbf{F} \quad (3.13)$$

Velocity gradient \mathbf{L} is defined by

$$\mathbf{L} = \text{grad} \mathbf{v} = \dot{\mathbf{F}} \mathbf{F}^{-1} \quad (3.14)$$

where the second relation follows from (3.6), (3.4) and (3.2). Symmetric or skew-symmetric parts of velocity gradient

$$\mathbf{D} \equiv \frac{1}{2}(\mathbf{L} + \mathbf{L}^T), \quad \mathbf{W} \equiv \frac{1}{2}(\mathbf{L} - \mathbf{L}^T), \quad \mathbf{L} = \mathbf{D} + \mathbf{W} \quad (3.15)$$

(where superscript T means transposition) we call *stretching* (or *rate of deformation*) \mathbf{D} or *spin* \mathbf{W} respectively. We note that (div and tr are divergence and trace, respectively)

$$\text{div} \mathbf{v} = \text{tr} \mathbf{L} = \text{tr} \mathbf{D} \quad (3.16)$$

Euler's relation is

$$\dot{J} = J \text{div} \mathbf{v} \quad (3.17)$$

which follows from (3.11), (3.12), (3.16) and from the properties of second order tensor function. ⁴

⁴ Tensors of 2nd order \mathbf{A} are linear transformations (matrix 3×3) of vector \mathbf{a} to vector \mathbf{b}

$$\begin{aligned} \mathbf{b} &= \mathbf{A} \mathbf{a} \\ b^i &= A^{ij} a^j \end{aligned} \quad (a)$$

where the second expression is in Cartesian components (with summation rule of course).

But vectors and tensors are more than matrices 3×1 and 3×3 : changing (Cartesian) coordinates by orthogonal matrix Q^{kl} (cf. Rem. 8) the components b^i of vector \mathbf{b} transforms into new (starred) components b^{*j} of the same vector \mathbf{b} by

$$b^{*j} = Q^{ji} b^i \quad (b)$$

That is, \mathbf{b} is the same “arrow” looked at from these different (starred and original) coordinates. Transformation (b) is valid for the usual *polar* vectors (less usual *axial* vectors, e.g., those obtainable by vector product [16], are discussed in Rem. 10). Similarly, the components A^{ij}

A motion is said to be *rigid* if the distances between the particles do not change in time.⁵ *Killing's theorem* asserts that motion of the body is rigid if and only if stretching is zero in all its particles

$$\mathbf{D} = \mathbf{0} \quad (3.18)$$

This follows from the definition of rigid motion (3.11)–(3.13) and from the very definition of material derivative (quadratic form with skew-symmetric tensor \mathbf{W} is zero):

$$0 = \overline{|\dot{\mathbf{d}}\mathbf{x}|^2} = \overline{\dot{\mathbf{d}}\mathbf{x} \cdot \dot{\mathbf{d}}\mathbf{x}} = 2\overline{\dot{\mathbf{d}}\mathbf{x} \cdot \mathbf{d}\mathbf{x}} = 2\overline{\dot{\mathbf{F}}\mathbf{d}\mathbf{X} \cdot \mathbf{d}\mathbf{x}} = 2\overline{\mathbf{L}\mathbf{d}\mathbf{x} \cdot \mathbf{d}\mathbf{x}} = 2\overline{\mathbf{D}\mathbf{d}\mathbf{x} \cdot \mathbf{d}\mathbf{x}}$$

As a *material volume* we denote such volume which contains the same particles during the motion. Therefore, configurations of a given body or its parts occupy material volumes. Similarly, material surface and material line are defined. It follows from properties of (3.1) that material volume, surface, or line are those in any

(Footnote 4 continued)

of tensor \mathbf{A} transform into starred components A^{*kl} of the same \mathbf{A} by

$$A^{*kl} = Q^{ki} A^{ij} Q^{lj} \quad (c)$$

(namely, transformation (c) guarantees linear transformation (a) with both vectors transformed by (b)).

Relations (b), (c) inspire in Sect. 3.2 the more general notion of changes of frame and frame indifference, cf. (3.31), (3.32).

Generalizations of tensors for nonCartesian coordinates see, e.g., [7, 16, 17] and Appendix A.4. Similar to matrices (3×3), tensors may be symmetric, skew-symmetric, etc., about vector and outer products. See Rems. 6, 16.

If $\mathbf{A} = \mathbf{A}(t)$ is a *tensor* function of the scalar t then $\det \mathbf{A}$ is the scalar function of t . Its derivative is

$$\frac{d \det \mathbf{A}}{dt} = \frac{\partial \det \mathbf{A}}{\partial A^{ij}} \frac{dA^{ij}}{dt} = (\det \mathbf{A}) \frac{dA^{ij}}{dt} A^{ji^{-1}} \quad (d)$$

where we use the following derivative of $\det \mathbf{A}$ with respect to its components (using its development according to line)

$$\frac{\partial \det \mathbf{A}}{\partial A^{ij}} = (\det \mathbf{A}) A^{ji^{-1}} \quad (e)$$

⁵ Rigid motion (3.1) has the general form

$$\mathbf{x} = \underline{\Theta} \mathbf{X} + \underline{\gamma}$$

where $\underline{\Theta}(t)$ and $\underline{\gamma}(t)$ are some orthogonal (Rem. 8) and vector functions of time t respectively. This follows from the preservation of distances of any two particles in reference \mathbf{X} , \mathbf{X}_0 and in actual configurations (positions \mathbf{x} , \mathbf{x}_0) in rigid motion, i.e.,

$$\mathbf{x} - \mathbf{x}_0 = \underline{\Theta}(\mathbf{X} - \mathbf{X}_0)$$

where orthogonal $\underline{\Theta}$ and \mathbf{x}_0 are arbitrary time function, cf. analogous deduction of (3.25).

configuration even if their magnitude or shape changes. An element of material volume dV in reference configuration transforms into an element of material volume dv in actual configuration by

$$dv = J dV \quad (3.19)$$

Indeed, if we express such elements as parallepipeds with $d\mathbf{X}_a$ or $d\mathbf{x}_a$ ($a = 1, 2, 3$) in reference or actual configurations, respectively, their volumes are given by triple products

$$dv = | \varepsilon^{ijk} dx_1^i dx_2^j dx_3^k |, \quad dV = | \varepsilon^{JKL} dX_1^J dX_2^K dX_3^L | \quad (3.20)$$

where ε^{ijk} (or ε^{JKL}) is the *permutation* or *Levi-Civita symbol*.⁶

Inserting (3.11) into (3.20), (both elementary volumes contain the same particles) and using the property of $\det \mathbf{A}$ from the end of Remark 6, Eq. (3.19) follows.

If $\psi(\mathbf{x}, t)$ has a meaning of the density of some quantity Ψ , then (at given instant)

$$\Psi = \int_{\mathcal{V}} \psi(\mathbf{x}, t) dv = \int_{\mathcal{V}_0} \psi(\mathbf{X}, t) J dV = \Psi(t) \quad (3.21)$$

where \mathcal{V}_0 is a material volume in reference configuration which in an actual one takes the material volume \mathcal{V} . The relation (3.21)₂ expresses the change of integral variables from actual to reference configuration.⁷

Now we can use the material derivative on the material volume: it is a time derivative of quantity (3.21) when the number of particles is constant

⁶ (In fact a cubic matrix) defined by

$$\varepsilon^{123} = \varepsilon^{231} = \varepsilon^{312} = 1$$

$$\varepsilon^{132} = \varepsilon^{213} = \varepsilon^{321} = -1$$

(the remaining elements of this $3 \times 3 \times 3$ matrix are zero)

From this definition, it follows (by direct calculation) the following properties of the permutation symbol (and its relation to Kronecker delta δ^{ij})

$$\varepsilon^{ijk} = \varepsilon^{jki} = \varepsilon^{kij} = -\varepsilon^{kji} = -\varepsilon^{jik} = -\varepsilon^{ikj}$$

(such “cyclic” permutation does not change its value)

$$\varepsilon^{ijk} \varepsilon^{ilm} = \delta^{jl} \delta^{km} - \delta^{jm} \delta^{kl}, \quad \varepsilon^{ijk} \varepsilon^{jkn} = 2\delta^{in}, \quad \varepsilon^{ijk} \varepsilon^{ijk} = 6$$

With this symbol we can express the *vector* and *triple products* as ($\mathbf{a}, \mathbf{b}, \mathbf{c}$ are vectors)

$$(\mathbf{a} \times \mathbf{b})^i = \varepsilon^{ijk} a^j b^k, \quad \mathbf{c} \cdot (\mathbf{a} \times \mathbf{b}) = \varepsilon^{ijk} c^i a^j b^k$$

and for the determinant of matrix \mathbf{A} it is valid that

$$\varepsilon^{ijk} A^{im} A^{jn} A^{kp} = \varepsilon^{mnp} \det \mathbf{A}$$

See also Rems. 4, 10, 16.

⁷ The density ψ may be deduced assuming Ψ as primitive and continuous with volume, i.e., when $\mathcal{V} \rightarrow 0$ also $\Psi \rightarrow 0$ [7, 10, 18–20].

$$\begin{aligned}
\overline{\int_{\mathcal{V}} \dot{\psi} \, dv} &= \overline{\int_{\mathcal{V}_0} \dot{\psi} J \, dV} = \overline{\int_{\mathcal{V}_0} \dot{\bar{\psi}} \bar{J} \, dV} = \int_{\mathcal{V}_0} (\dot{\bar{\psi}} J + \bar{J} \dot{\psi}) \, dV \\
&= \int_{\mathcal{V}_0} (\dot{\bar{\psi}} + \bar{\psi} \operatorname{div} \mathbf{v}) J \, dV = \int_{\mathcal{V}} (\dot{\bar{\psi}} + \bar{\psi} \operatorname{div} \mathbf{v}) \, dv = \int_{\mathcal{V}} \frac{\partial \bar{\psi}}{\partial t} \, dv \\
&\quad + \int_{\mathcal{V}} (\operatorname{div} \bar{\psi} \mathbf{v}) \, dv
\end{aligned} \tag{3.22}$$

Here (3.19), (3.21), the independence of the reference configuration on time, (3.17), (3.8) were used.

Using Gauss' theorem

$$\int_{\mathcal{V}} (\operatorname{div} \bar{\psi} \mathbf{v}) \, dv = \int_{\partial \mathcal{V}} \bar{\psi} \mathbf{v} \cdot \mathbf{n} \, da \tag{3.23}$$

(where \mathbf{n} is an outside normal and da is an element of the material surface $\partial \mathcal{V}$ of material volume \mathcal{V} in actual configuration) we obtain from (3.22) the *Reynolds theorem*

$$\overline{\int_{\mathcal{V}} \dot{\psi} \, dv} = \int_{\mathcal{V}} \frac{\partial \bar{\psi}}{\partial t} \, dv + \int_{\partial \mathcal{V}} \bar{\psi} \mathbf{v} \cdot \mathbf{n} \, da = \frac{d}{dt} \int_{\mathcal{V}} \bar{\psi} \, dv + \int_{\partial \mathcal{V}} \bar{\psi} \mathbf{v} \cdot \mathbf{n} \, da \tag{3.24}$$

where the last expression follows for the fixed volume V with fixed surface ∂V (i.e., this geometrical object is not changed in time) which at a given instant coincides with material volume \mathcal{V} .

Therefore, the Reynolds theorem asserts that the rate of change of quantity ψ in a material volume \mathcal{V} in a given instant is equal to the rate of its change in a fixed volume V (coincided with \mathcal{V} in that instant) and the flow of such a quantity through its fixed surface ∂V . Consequently, it expresses the natural change from closed to open system in continuum theory where ψ is sufficiently smooth and \mathcal{V} is a volume of any part inside the body (cf. solidification principle in Sect. 3.3 and Rems. 14 in Chap. 2, 23 in this chapter, 11 in Chap. 4). The Reynolds theorem may be generalized on a surface moving with arbitrary fictive velocity [13].

Summary. Mathematical basis for the description of space changes or effects is presented. They are based on calculus with vectors and tensors (usually of the second order) and their functions. The most important concepts or quantities are the two derivatives—time and space, cf. (3.5) and the notation above it, and (3.8)—the velocity gradient (3.14) and its decomposition (3.15), and the density of some physical quantity (3.21). It is also essential to realize the difference between the

(Footnote 7 continued)

The additivity of Ψ in volume (Ψ for volume consisting of two separate volumes is the sum of Ψ of each separate volume) follows from (3.21). Such quantities Ψ are usual in continuum thermomechanics, cf. mass, energy, entropy, etc.; using mass and mass density we can introduce specific quantities instead of densities (cf. (3.66) and Sects. 3.4, 4.6) and extensivity instead of additivity (cf. Sects. 1.2, 2.4). Similarly, [19, 20] there are quantities continuous in surface with surface densities (cf. (3.58), (3.99) and Rems. 14, 18).

actual and the material volume (see the paragraph above (3.19) and to understand related derivatives of volume integrals in (3.22) and (3.24)).

3.2 Change of Frame

It was assumed so far that the frame in which we observe our thermodynamic system in actual configuration is fixed. *Frame* is a set of objects the mutual distances of which do not change (like the walls of a laboratory, arms of the rotor of a centrifuge, distant stars, or any body in rigid motion) and which are combined with some clock. An observed *event* in the actual configuration is characterized by a place (position vector) \mathbf{x} and an instant t and the same event may be described in a different “starred” frame by place \mathbf{x}^* and instant t^* . Some frames—those which are inertial—play a special role (see below and Sect. 3.3), but more important is the change of frame in actual configurations (reference configuration is not influenced by it) [7, 10, 12, 21–24] (for generalization, see end of Sect. 3.4).

Change of frame from the original frame to a new “starred” one is given by

$$\mathbf{x}^* = \mathbf{c}(t) + \mathbf{Q}(t)\mathbf{x}, \quad x^{*j} = c^j(t) + Q^{ji}(t)x^i \quad (3.25)$$

$$t^* = t + b \quad (3.26)$$

Here, the function $\mathbf{c}(t)$ or $\mathbf{Q}(t)$ of time t (cf. under (3.119)) give vectors or orthogonal tensors,⁸ respectively, and b is a scalar constant. In actual reference, the x^i or x^{*j} are Cartesian components of the same event in a Cartesian coordinate system fixed with an old (original) or new (starred) frame, respectively: in the Cartesian system of a new frame at given instant t , c^j and $Q^{ji}x^i$ are the positions of origin and of event (seen in the Cartesian system of the old frame), respectively, cf. Fig. 3.1.

Transformations (3.25) and (3.26) follow from the expected properties of the change of frame in classical physics: the distance between two simultaneous events

⁸ Orthogonal tensor \mathbf{Q} transforms any vector \mathbf{a} into vector \mathbf{Qa} of the same length $\mathbf{a} \cdot \mathbf{a} = \mathbf{Qa} \cdot \mathbf{Qa}$. Then the basic properties of orthogonal tensor \mathbf{Q} follow:

$$\mathbf{Q}^T \mathbf{Q} = \mathbf{Q} \mathbf{Q}^T = \mathbf{1}, \quad \text{in components } Q^{ki} Q^{kj} = Q^{ik} Q^{jk} = \delta^{ij}$$

$$\mathbf{Q}^{-1} = \mathbf{Q}^T, \quad (\det \mathbf{Q})^2 = 1$$

An example of the orthogonal tensor is (3.29).

Orthogonal transformations \mathbf{Q} form a group: generally (cf. [9, 15, 16]) a set of elements with a defined “product” giving another element from this set (here a matrix product of two orthogonal tensors giving again an orthogonal tensor) with inverse and unit elements (here \mathbf{Q}^T and $\mathbf{1}$ respectively). This group is called a *full orthogonal group* with $\det \mathbf{Q} = \pm 1$ which expresses rotation or/and reflection. A *proper orthogonal group* forms its subgroup with $\det \mathbf{Q} = +1$ (a subgroup is a subset with group properties again).

The corresponding orthogonal matrix Q^{ij} may be also used for rotation (and/or inversion) of Cartesian coordinates, cf. (b), (c) in Rem. 4 and Rem. 10.

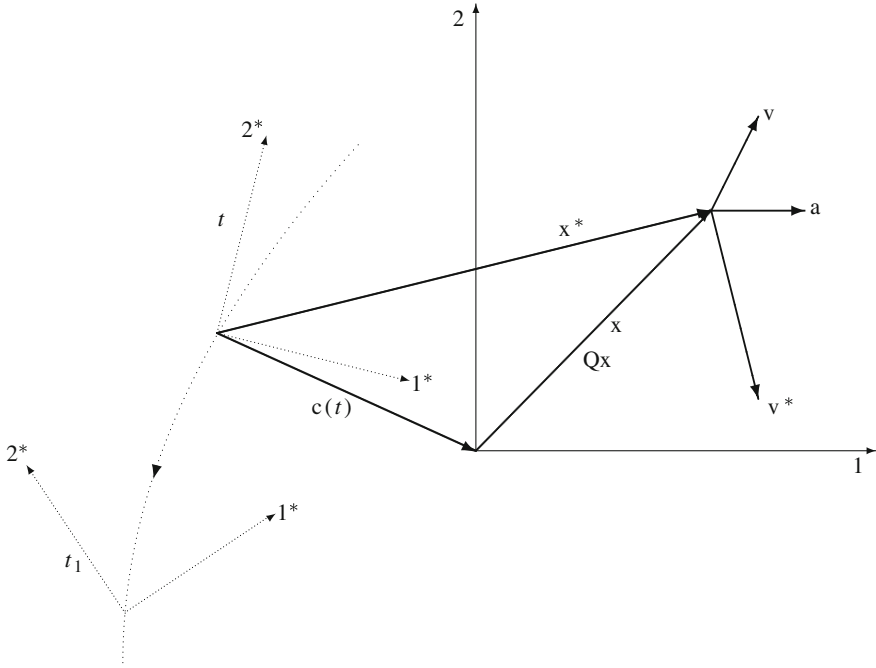


Fig. 3.1 On relationships between two frames

is preserved and the time interval between two events and the time order of events is left unchanged. Indeed [12, 14, 22], let us consider two simultaneous events taking place \mathbf{x} and \mathbf{x}_0 in the original frame and \mathbf{x}^* and \mathbf{x}_0^* in the new, “starred” frame. Because their distance must be preserved $|\mathbf{x} - \mathbf{x}_0| = |\mathbf{x}^* - \mathbf{x}_0^*|$, vectors in this equation must be connected by orthogonal transformation \mathbf{Q} (see Rem. 8), i.e., $\mathbf{x}^* - \mathbf{x}_0^* = \mathbf{Q}(\mathbf{x} - \mathbf{x}_0)$. Taking $\mathbf{c} \equiv \mathbf{x}_0^* - \mathbf{Q}\mathbf{x}_0$ we obtain (3.25) because both frames are moving each to the other generally not steadily and therefore, \mathbf{c} and \mathbf{Q} are functions of time (see Fig. 3.1) (this deduction is analogous to the deduction of rigid motion in Rem. 5, where distances are also preserved, see also discussion of (3.223) and Rem. 40). Further, let us consider two arbitrary events, the earlier and latter having their instants t_0 and t or t_0^* and t^* in the original or “starred” frame, respectively. From the preservation of the time interval, we have $|t - t_0| = |t^* - t_0^*|$ and from the preservation of the time order we have $t^* > t_0^*$ because of $t > t_0$. Then preceding equality gives $t^* - t_0^* = t - t_0$, i.e., (3.26) if we choose $b \equiv t_0^* - t_0$.

It is evident from (3.25) and (3.26) that b is the time shift in the origin of the time axes, \mathbf{c} is the shift in the origins of the Cartesian systems and \mathbf{Q} (from full orthogonal group, cf. Rem. 8) expresses the rotation ($\det \mathbf{Q} = 1$) or reflection ($\det \mathbf{Q} = -1$) of the starred frame relative to the original one.⁹ We also note the inversions of change

⁹ Use of a full or proper orthogonal group puts the additional property of preservation of right- or left handedness on the change of frame; some authors [12, 23–26] (motivated usually

of frame (3.25), (3.26)

$$\mathbf{x} = \mathbf{Q}^T(t)(\mathbf{x}^* - \mathbf{c}(t)) \quad (3.27)$$

$$t = t^* - b \quad (3.28)$$

The change of frames (3.25), (3.26) and its consequences below is also demonstrated in the following example of centrifuge: We take as an original frame the walls of the laboratory and as a new “starred” frame the rotor of centrifuge, having a constant number $\omega/2\pi$ of revolutions in the time unit (ω is the angular velocity) and rotating from the first to the second axis around the third axis of original frame. Here, (3.25) is

$${}^*x^j = Q^{ji}(t)x^i, \quad \|\mathbf{Q}^{ij}(t)\| = \begin{pmatrix} \cos\omega t & \sin\omega t & 0 \\ -\sin\omega t & \cos\omega t & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (3.29)$$

with corresponding orthogonal time function. There is also no shift in space and time origins: $c^j(t) \equiv 0$ and $b = 0$ in (3.25) and (3.26) respectively. Other results concerning centrifuge are noted below (3.41) and below (3.46).

The special case of (3.25) is the *Galileo transformation* where function $\mathbf{c}(t)$ is linear and \mathbf{Q} is a constant, i.e., frames are moving each to the other with constant velocity and differ by a constant angle (or also by inversion). A special set of frames must be noted—*inertial frames* which contain the frame formed by distant stars and those obtained from it by Galileo transformation (cf. Sects. 3.3, 4.3; in many applications the frame fixed with earth surface may be taken as an approximately inertial one). Their typical property is zero inertial acceleration (3.48).

A more special case with $\mathbf{c} = \mathbf{o}$ and \mathbf{Q} constant is physically trivial because it expresses the change of coordinate system only. Therefore, a change of coordinates (in Rem. 4) is not the same as the much more general change of frame (where time and its transformation (3.26) and shifts in origins are moreover considered).

Many quantities used in the following considerations are called *objective* or *frame-indifferent*, if they are “invariant” in the change of frame (3.25), (3.26) as follows (because this change contains rotations and/or inversions of corresponding Cartesian systems as a very special case (cf. Fig. 3.1), the following definition is motivated by (b), (c) of Rem. 4):

Objective or frame-indifferent scalar a , vector \mathbf{a} and (second order) tensor \mathbf{A} transform by the change of frame on scalar a^* , vector \mathbf{a}^* and tensor \mathbf{A}^* as follows:

$$a^* = a \quad (3.30)$$

$$\mathbf{a}^* = \mathbf{Q}\mathbf{a} \quad (3.31)$$

(Footnote 9 continued)

by nonmechanical arguments) confine (3.25) only to the rotations. This problem seems not to have been settled. Because it has no influence on the linear models preferred here, we use in the following the full orthogonal group, see Appendix A.2.

$$\mathbf{A}^* = \mathbf{Q}\mathbf{A}\mathbf{Q}^T \quad (3.32)$$

This is because an objective scalar a does not change its value, objective vector \mathbf{a} is the same “arrow” looked at from different frames and, ultimately, an objective tensor \mathbf{A} transforms an objective vector (say \mathbf{a}_1) to an objective vector (say \mathbf{a}_2) in all frames: indeed if in the original frame $\mathbf{a}_2 = \mathbf{A}\mathbf{a}_1$ and in the “starred” frame $\mathbf{a}_2^* = \mathbf{A}^*\mathbf{a}_1^*$ then by (3.31) we obtain (3.32).

But there are also quantities which are nonobjective, i.e., they do not transform by (3.30)–(3.32) when the frame is changed. Generally, we can find the transformation of any quantity at the transformation of t, \mathbf{x} to t^*, \mathbf{x}^* and vice versa according to (3.25), (3.26), (3.27), (3.28), i.e., to decide about objectivity or nonobjectivity (frame indifference or not) according to the following nearly obvious precepts:

- The reference configuration and its properties (like particles and bodies in reference) are not influenced by changing of frame (this affects actual references only).
- For primitives we must decide about their objectivity (frame indifference) a priori (e.g., it may be expected that primitives of this Chap. 3 connected with the body, like density, temperature, internal energy, entropy, etc., are objective).
- For the other defined quantities, we decide from their definitions assuming that the definition itself is not influenced by change of frame (i.e., definitions are the same in any frame). Not only those, but in fact all relations between quantities (e.g., those from Sect. 3.1) are valid also for new (starred) frame, i.e., for new starred quantities if we use t^*, \mathbf{x}^* (3.25), (3.26) simultaneously. This is evident from the fact that the frame used for actual reference (say in Sect. 3.1) was chosen quite arbitrarily. Cf. also end of this section.

Applying the change of frame (3.25), (3.26) to the above definitions of Sect. 3.1 and, using these precepts, we can decide about objectivity or nonobjectivity (frame indifference or not) of the following quantities (more detailed proofs of some of them are written in the footnote-sized script below); the remainder from the next sections may be proved analogously.

It follows from (3.25), (3.26) that time t and place \mathbf{x} are not objective because these scalar and vector do not transform as prescribed by (3.30), (3.31) (but time and space intervals are objective).

Motion (3.1) transforms as

$$\underline{\chi}^*(\mathbf{X}, \mathbf{t}^*) = \mathbf{c}(\mathbf{t}) + \mathbf{Q}(\mathbf{t}) \underline{\chi}(\mathbf{X}, \mathbf{t}) \quad (3.33)$$

and therefore it is not an objective vector (cf. objective (3.31), (3.56))

Proof Motion (3.1) in the starred frame is by (3.25), (3.28)

$$\overset{*j}{\chi}(\mathbf{X}, t^*) = \overset{*j}{x} = c^j(t^* - b) + Q^{ji}(t^* - b) \chi^i(\mathbf{X}, t^* - b) \quad (3.34)$$

(particle \mathbf{X} is not influenced) which is nonobjective (3.33). Q.E.D.

Velocity \mathbf{v} is transformed as

$$\mathbf{v}^* = \mathbf{Q}\mathbf{v} + \dot{\mathbf{c}} + \dot{\mathbf{Q}}\mathbf{x} \quad (3.35)$$

and therefore it is not an objective vector.

Proof Velocity (3.7) in the new starred frame is (using (3.34))

$$\begin{aligned} v^{*j} &\equiv \frac{\partial \chi^j(X^J, t^*)}{\partial t^*} = \frac{\partial (c^j(t^* - b) + Q^{ji}(t^* - b)\chi^i(X^J, t^* - b))}{\partial t^*} \\ &= \frac{dc^j(t)}{dt} \frac{d(t^* - b)}{dt^*} + \frac{dQ^{ji}(t)}{dt} \frac{d(t^* - b)}{dt^*} \chi^i(X^J, t) + Q^{ji}(t) \frac{\partial \chi^i(X^J, t)}{\partial t} \frac{d(t^* - b)}{dt^*} \\ &= Q^{ji}(t)v^i(X^J, t) + \dot{c}^j(t) + \dot{Q}^{ji}(t)\chi^i(X^J, t) \end{aligned} \quad (3.36)$$

which is (3.35) by (3.1); here

$$\dot{c}^j = \frac{dc^j(t)}{dt}, \quad \dot{Q}^{ji} = \frac{dQ^{ji}(t)}{dt}, \quad \frac{d(t^* - b)}{dt^*} = 1 \quad (3.37)$$

have been used. Q.E.D.

This (3.35) may be written by (3.27)

$$\mathbf{v}^* = \mathbf{Q}\mathbf{v} + \dot{\mathbf{c}} + \underline{\underline{\Omega}}(\mathbf{x}^* - \mathbf{c}) \quad (3.38)$$

where (tensor of) angular velocity $\underline{\underline{\Omega}}$ (of original frame relative to the new one) is defined as

$$\underline{\underline{\Omega}} \equiv \dot{\mathbf{Q}}\mathbf{Q}^T \quad (3.39)$$

and this tensor is skew-symmetric (this follows from time derivative of $\mathbf{Q}\mathbf{Q}^T = \mathbf{1}$, namely $\dot{\mathbf{Q}}\mathbf{Q}^T + \mathbf{Q}\dot{\mathbf{Q}}^T = \dot{\mathbf{Q}}\mathbf{Q}^T + (\dot{\mathbf{Q}}\mathbf{Q}^T)^T = \mathbf{0}$ which is zero tensor).

By inversion of (3.38) and by (3.39), (3.25), Rem. 8

$$\mathbf{v} = \mathbf{Q}^T\mathbf{v}^* - \mathbf{Q}^T\dot{\mathbf{c}} + \underline{\underline{\Omega}}^*\mathbf{x} \quad (3.40)$$

where we define the (tensor of) angular velocity $\underline{\underline{\Omega}}^*$ (of the new frame relative to the original one) by

$$\underline{\underline{\Omega}}^* = -\mathbf{Q}^T\underline{\underline{\Omega}}\mathbf{Q} \quad (3.41)$$

The origin of the name ‘‘angular velocity’’ for (3.39), (3.41) may be seen in the example of centrifuge (3.29): Calculation of tensors of angular velocities (3.39), (3.41) gives for this example $\Omega^{12} = \Omega^{*21} = \omega = -\Omega^{*12} = -\Omega^{21}$ (their other components are zero). Define the vector of angular velocity $\underline{\omega}$ as axial

one¹⁰ corresponding to skew-symmetric tensor $\underline{\underline{\Omega}}^*$ according to (b) in Rem. 10 as $\underline{\omega}^i = (1/2)\varepsilon^{ijk}\underline{\underline{\Omega}}^{*kj}$. This axial vector (changing parity it changes the sign) has only one nonzero component $\omega^3 = \omega$. From (3.40) for the point fixed on the rotor $\mathbf{v}^* = \mathbf{o}$ (we consider \mathbf{x} perpendicular to the rotation axis, $\mathbf{c}(\mathbf{t}) \equiv \mathbf{o}$) we obtain

$$\mathbf{v} = \underline{\underline{\Omega}}^* \mathbf{x}, \quad \mathbf{v} = \underline{\omega} \times \mathbf{x} \quad (3.42)$$

where the equivalent second relation (using the vector product) follows from (c) in Rem. 10 and the vector product noted in Rem. 6. This is in accord with the name of $\underline{\underline{\Omega}}^*$ because $\underline{\omega}$ is the vector of angular velocity of new frame (centrifuge) relative to the old one (laboratory).

Similarly, for point fixed in laboratory ($\mathbf{v} = \mathbf{o}$) we have by (3.38)

$$\mathbf{v}^* = \underline{\underline{\Omega}} \mathbf{x}^* \quad \text{or} \quad \mathbf{v}^* = -\underline{\omega} \times \mathbf{x}^* \quad (3.43)$$

($-\underline{\omega}$ is an axial vector equivalent to $\underline{\underline{\Omega}} : \Omega^{jk} = -\underline{\underline{\Omega}}^{*jk} = -\omega^i \varepsilon^{ikj}$). Acceleration $\dot{\mathbf{v}}$ is also not objective. Namely, by (3.38)

¹⁰ As distinct from usual polar vectors which by coordinate changes (characterized by orthogonal matrix Q^{ji} , see Rem. 8) transform by (b) of Rem. 4, the *axial vector* \mathbf{w} is defined by transformation

$$\underline{\underline{w}}^{*j} = (\det \mathbf{Q}) Q^{ji} w^i \quad (a)$$

and therefore changes the sign at parity (right-handedness or left-handedness) changes ($\det \mathbf{Q} = -1$, cf. Rem. 8)

Lemma (equivalency of skew-symmetric tensors with axial vectors): For every skew-symmetric tensor (of second order) \mathbf{W} it is possible to define an axial vector \mathbf{w} (both contain three (independent) components) and vice versa by

$$w^i = (1/2)\varepsilon^{ijk} W^{kj} \quad (b), \quad W^{jk} = w^i \varepsilon^{ikj} \quad (c)$$

Indeed, the usual coordinate transformation of tensor \mathbf{W} (i.e., of the type (c) in Rem. 4) leads to axiality transformation (a). Namely, (b) must be valid also for the new (starred) coordinate system

$$\underline{\underline{w}}^{*i} = (1/2)\varepsilon^{ijk} \underline{\underline{W}}^{*kj} = (1/2)\varepsilon^{ijk} Q^{kl} W^{lm} Q^{jm} = (1/2)\varepsilon^{ijk} Q^{kl} w^p \varepsilon^{pml} Q^{jm}$$

which multiplying by Q^{ir} gives

$$\underline{\underline{w}}^{*i} Q^{ir} = (1/2)w^p \varepsilon^{pml} \varepsilon^{ijk} Q^{ir} Q^{jm} Q^{kl} = (1/2)w^p \varepsilon^{pml} \varepsilon^{rml} (\det \mathbf{Q}) = (\det \mathbf{Q}) w^r$$

where properties of permutation symbol from Rem. 6 were used. Multiplying it by orthogonal Q^{jr} we obtain (a) and therefore \mathbf{w} is an axial vector.

Axiality of \mathbf{w} is automatically achieved by the usual transformation ((c) in Rem. 4) of tensor \mathbf{W} . Therefore the skew-symmetric tensors instead of axial vectors and outer product (see Rem. 16) may be used and we do it this way at the moment of momentum balances in the Sects. 3.3, 4.3, cf. [7, 8, 14, 27]. Generalization of this Lemma to third-order tensors, made by M. Šilhavý, is published in Appendix of [28].

$$\dot{\mathbf{v}}^* = \mathbf{Q}\dot{\mathbf{v}} + \dot{\mathbf{i}}^* \quad (3.44)$$

where $\dot{\mathbf{i}}^*$ is defined by

$$\dot{\mathbf{i}}^* \equiv 2\dot{\mathbf{Q}}\mathbf{v} + \ddot{\mathbf{c}} + \ddot{\mathbf{Q}}\mathbf{x} \quad (3.45)$$

Proof From the definition of acceleration in the new, starred frame and by (3.36), (3.28) we have

$$\begin{aligned} (\dot{v}^j)^* &\equiv \frac{\partial v^{*j}(X^J, t^*)}{\partial t^*} \\ &= \frac{\partial(Q^{ji}(t^* - b)v^i(X^J, t^* - b) + \dot{c}^j(t^* - b) + \dot{Q}^{ji}(t^* - b)\chi^i(X^J, t^* - b))}{\partial t^*} \\ &= Q^{ji}(t) \frac{\partial v^i(X^J, t)}{\partial t} + \frac{dQ^{ji}(t)}{dt} v^i(X^J, t) + \frac{d\dot{c}^j(t)}{dt} \\ &\quad + \frac{d\dot{Q}^{ji}(t)}{dt} \chi^i(X^J, t) + \dot{Q}^{ji}(t) \frac{\partial \chi^i(X^J, t)}{\partial t} \\ &= Q^{ji} \dot{v}^i + 2\dot{Q}^{ji} v^i + \ddot{c}^j + \ddot{Q}^{ji} x^i \end{aligned}$$

which is (3.44), (3.45) with (3.37) and

$$\ddot{c}^j = \frac{d\dot{c}^j(t)}{dt}, \quad \ddot{Q}^{ji} = \frac{d\dot{Q}^{ji}(t)}{dt}$$

Q.E.D.

This *inertial acceleration* $\dot{\mathbf{i}}^*$ (perceived in the new, starred frame) may be traditionally rewritten as (using (3.40), (3.41), (3.39), (3.27) and $\underline{\underline{\Omega}} + \underline{\underline{\Omega}}^2 = \underline{\underline{\Omega}} - \underline{\underline{\Omega}}\underline{\underline{\Omega}}^T = \underline{\underline{Q}}\underline{\underline{Q}}^T$)

$$\dot{\mathbf{i}}^* = 2\underline{\underline{\Omega}}(\mathbf{v}^* - \dot{\mathbf{c}}) - \underline{\underline{\Omega}}^2(\mathbf{x}^* - \mathbf{c}) + \underline{\underline{\Omega}}(\mathbf{x}^* - \mathbf{c}) + \ddot{\mathbf{c}} \quad (3.46)$$

The terms on the right-hand side of (3.46) are, subsequently, the Coriolis, centrifugal, and Euler accelerations and the last term is the acceleration of the origin.

For example of centrifuge (3.29) above (angular velocity is constant in time) the inertial acceleration $\dot{\mathbf{i}}^*$ (3.46) in the place \mathbf{x}^* perpendicular to the rotation axis and fixed with the rotor (starred frame, $\mathbf{v}^* = \mathbf{o}$) is therefore only the centrifugal one (see below (3.43) and Rem. 6)

$$\dot{\mathbf{i}}^* = -\underline{\underline{\Omega}}^2 \mathbf{x}^* = \omega^2 \mathbf{x}^* \quad (3.47)$$

Note that in Galileo transformation ($\mathbf{c}(t)$ linear, \mathbf{Q} constant)

$$\dot{\mathbf{i}}^* = \mathbf{o} \quad (3.48)$$

This zero inertial acceleration is assumed in the frame fixed with distant stars and therefore also in any inertial frame and at change between them. Therefore, in inertial

frames the identity (3.48) is valid and the acceleration $\dot{\mathbf{v}}$ behaves objectively (frame indifferently).

Applying the change of frame (3.25), (3.26) on the further definitions of Sect. 3.1 and using the three precepts above we can decide about their frame indifference (objectivity); those remaining may be proved analogously.

Deformation gradient \mathbf{F} (3.10) is not a frame-indifferent (objective) tensor, because it transforms as

$$\mathbf{F}^* = \mathbf{Q}\mathbf{F} \quad (3.49)$$

Namely, deformation gradient (3.10) in starred frame transforms by (3.33), (3.28)

$$\begin{aligned} {}^{*jJ}F &\equiv \partial \chi^*(X^K, t^*) / \partial X^J = \partial (c^j(t^* - b) + Q^{ji}(t^* - b)\chi^i(X^K, t^* - b)) / \partial X^J \\ &= Q^{ji}(t)\partial \chi^i(X^K, t) / \partial X^J = Q^{ji}F^{iJ} \end{aligned}$$

But the scalar J defined by (3.12) is the objective one

$$J^* \equiv |\det \mathbf{F}^*| = |\det \mathbf{Q}| |\det \mathbf{F}| = |\det \mathbf{F}| = J \quad (3.50)$$

Obviously, $\text{Grad} \mathbf{F}$ is an objective vector (cf. e.g., [28, 29])

$$(\text{Grad} \mathbf{F})^* = \mathbf{Q} \text{Grad} \mathbf{F} \quad (3.51)$$

(at fixed reference, \mathbf{F} and $\text{Grad} \mathbf{F}$ may be considered as objective vectors (3.31), cf. (3.122)).

The velocity gradient \mathbf{L} (3.14) is transformed at frame change as

$$\mathbf{L}^* = \mathbf{Q}\mathbf{L}\mathbf{Q}^T + \underline{\Omega} \quad (3.52)$$

and therefore it is not an objective tensor (recall the skew-symmetry of $\underline{\Omega}$ (3.39)).

Proof We write transformation of velocity (3.38) in actual (Euler) description and use (3.27), (3.28):

$$\begin{aligned} {}^{*i}v({}^{*l}x, t^*) &= Q^{ik}(t)v^k(x^l, t) + \dot{c}^i(t) + \Omega^{ik}(t)(x^{*k} - c^k(t)) \\ &= Q^{ik}(t^* - b)v^k(Q^{ml}(t^* - b)(x^{*m} - c^m(t^* - b)), t^* - b) \\ &\quad + \dot{c}^i(t^* - b) + \Omega^{ik}(t^* - b)(x^{*k} - c^k(t^* - b)) \end{aligned}$$

Using this and starting with definition (3.14) in the new, starred frame we obtain

$$\begin{aligned}
L^{*ij}(x^*, t^*) &\equiv \frac{\partial v^{*i}(x^*, t^*)}{\partial x^{*j}} = Q^{ik}(t^* - b) \frac{\partial v^k(Q^{ml}(t^* - b)(x^{*m} - c^m(t^* - b)), t^* - b)}{\partial x^{*j}} \\
&\quad + \Omega^{ik}(t^* - b) \frac{\partial (x^{*k} - c^k(t^* - b))}{\partial x^{*j}} \\
&= Q^{ik}(t) \frac{\partial v^k(x^l, t)}{\partial x^n} \frac{\partial (Q^{mn}(t^* - b)(x^{*m} - c^m(t^* - b)))}{\partial x^{*j}} + \Omega^{ik}(t^* - b) \delta^{kj} \\
&= Q^{ik}(t) L^{kn}(x^l, t) Q^{mj}(t) \delta^{mj} + \Omega^{ij}(t) = Q^{ik}(t) L^{kn}(x^l, t) Q^{jn}(t) + \Omega^{ij}(t)
\end{aligned}$$

and this is (3.52). Q.E.D.

Using (3.15) in the starred frame we find with (3.52) that the spin \mathbf{W} is not objective

$$\mathbf{W}^* = \mathbf{Q}\mathbf{W}\mathbf{Q}^T + \underline{\Omega} \quad (3.53)$$

but the stretching tensor \mathbf{D} is objective (frame indifferent)

$$\mathbf{D}^* = \mathbf{Q}\mathbf{D}\mathbf{Q}^T \quad (3.54)$$

Transformation properties of some objects (mostly derivatives useful in the following chapters) formed from scalar a , vector \mathbf{a} , tensor \mathbf{A} which are objective (frame indifferent) (3.30)–(3.32), will be discussed now. We must realize that these objective conditions must be valid at any \mathbf{x}^* , t^* transforming by (3.25), (3.26) to \mathbf{x} , t (the same event seen from different frames passing at the same particle \mathbf{X}); therefore¹¹

$$a^*(\mathbf{X}, t^*) = a^*(\mathbf{x}^*, t^*) = a^* = a = a(\mathbf{x}, t) = a(\mathbf{X}, t) \quad (3.55)$$

$$\mathbf{a}^*(\mathbf{X}, t^*) = \mathbf{a}^*(\mathbf{x}^*, t^*) = \mathbf{a}^* = \mathbf{Q}\mathbf{a} = \mathbf{Q}(t)\mathbf{a}(\mathbf{x}, t) = \mathbf{Q}(t)\mathbf{a}(\mathbf{X}, t) \quad (3.56)$$

$$\mathbf{A}^*(\mathbf{x}^*, t^*) = \mathbf{A}^* = \mathbf{Q}\mathbf{A}\mathbf{Q}^T = \mathbf{Q}(t)\mathbf{A}(\mathbf{x}, t)\mathbf{Q}^T(t) \quad (3.57)$$

As a result, we obtain: If scalar a is objective (3.55) then its material derivative \dot{a} and space gradient $\text{grad}a$ are objective while $\text{Grad}a$ and $\partial a/\partial t$ are not. If \mathbf{a} is an objective vector, $\text{div}\mathbf{a}$, $\mathbf{a}\cdot\mathbf{a} = \mathbf{a}^2$ are objective, while material derivative $\dot{\mathbf{a}}$ is not. Ultimately, with objective (second order) tensor \mathbf{A} , the vector $\text{div}\mathbf{A}$ and the scalars $\text{tr}\mathbf{A}$, $\det\mathbf{A}$ are objective.

Proofs Transformation (frame change) of objective scalar a (3.55) with (3.28) gives the objectivity of scalar material derivative

¹¹ Note that functions on both sides of (3.55)₁ are different: $a^*(\mathbf{x}^*, t^*) = a^*(\chi^*(\mathbf{X}, t^*), t^*) \equiv a^*(\mathbf{X}, t^*)$. Remark that the assumption (3.30) is crucial for validity of (3.55); namely, the function $\alpha(\mathbf{x}, t)$, defined by (3.25), (3.26) as $a^*(\mathbf{x}^*, t^*) = a^*(\mathbf{c} + \mathbf{Q}\mathbf{x}, t + b) \equiv \alpha(\mathbf{x}, t)$ is generally different from function $a(\mathbf{x}, t)$. Similarly (3.31) and (3.32) are crucial for (3.56) and (3.57).

$$(\dot{a})^* \equiv \frac{\partial a^*(X^K, t^*)}{\partial t^*} = \frac{\partial a(X^L, t^* - b)}{\partial t^*} = \frac{\partial a(X^L, t)}{\partial t} \frac{d(t^* - b)}{dt^*} = \dot{a}$$

and also objectivity of vector grada (by (3.27), (3.28))

$$\begin{aligned} (\text{grada})^{*j} &\equiv \frac{\partial a^*(x^{*m}, t^*)}{\partial x^{*j}} \\ &= \frac{\partial a(x^n, t)}{\partial x^{*j}} = \frac{\partial a(Q^{pn}(t^* - b)(x^{*P} - c^P(t^* - b)), t^* - b)}{\partial x^{*j}} \\ &= \frac{\partial a(x^n, t)}{\partial x^i} \frac{\partial(Q^{pi}(t^* - b)(x^{*P} - c^P(t^* - b)))}{\partial x^{*j}} \\ &= \frac{\partial a(x^n, t)}{\partial x^i} Q^{ji}(t) = Q^{ji}(\text{grada})^i \end{aligned}$$

But the vector Grada is not objective because

$$(\text{Grada})^J \equiv \frac{\partial a^*(X^K, t^*)}{\partial X^J} = \frac{\partial a(X^L, t)}{\partial X^J} = (\text{Grada})^J$$

as well as $\partial a/\partial t$ (by (3.28), (3.27))

$$\begin{aligned} (\partial a/\partial t)^* &\equiv \frac{\partial a^*(x^{*m}, t^*)}{\partial t^*} = \frac{\partial a(x^n, t)}{\partial t^*} = \frac{\partial a(Q^{pn}(t^* - b)(x^{*P} - c^P(t^* - b)), t^* - b)}{\partial t^*} \\ &= \frac{\partial a(x^n, t)}{\partial t} \frac{d(t^* - b)}{dt^*} + \frac{\partial a(x^n, t)}{\partial x^i} \frac{\partial(Q^{pi}(t^* - b)(x^{*P} - c^P(t^* - b)))}{\partial t^*} \\ &= \frac{\partial a(x^n, t)}{\partial t} + \frac{\partial a(x^n, t)}{\partial x^i} \left(\frac{dQ^{pi}(t)}{dt} (x^{*P} - c^P(t^* - b)) - Q^{pi}(t) \frac{dc^P(t)}{dt} \right) \\ &= \frac{\partial a}{\partial t} + (\text{grada})^i (\dot{Q}^{pi} Q^{pj} x^j - Q^{pi} \dot{c}^P) \end{aligned}$$

or (using time derivative of $Q^{pi} Q^{pj} = \delta^{ij}$)

$$(\partial a/\partial t)^* = \partial a/\partial t - Q^{pi}(\text{grada})^i (\dot{Q}^{pj} x^j + \dot{c}^P)$$

i.e. the (space) time derivative of objective scalar a is not the objective scalar.

Transformation (frame change) of objective vector \mathbf{a} (3.56) gives the objectivity of the scalar product \mathbf{a}^2

$$(\mathbf{a}^2)^* \equiv \mathbf{a}^* \cdot \mathbf{a}^* = a^{*i} a^{*i} = Q^{ij} a^j Q^{ik} a^k = \delta^{jk} a^j a^k = a^j a^j = \mathbf{a} \cdot \mathbf{a} = \mathbf{a}^2$$

and also the objectivity of the (space) divergence $\text{div} \mathbf{a}$ (scalar) using (3.27), (3.28), Rem. 8

$$\begin{aligned}
 (\text{div} \mathbf{a})^* &\equiv \frac{\partial a^i(x^*, t^*)}{\partial x^i} = \frac{\partial(Q^{ij}(t)a^j(x^m, t))}{\partial x^i} \\
 &= \frac{\partial(Q^{ij}(t^* - b)a^j(Q^{nm}(t^* - b)(x^{*n} - c^n(t^* - b)), t^* - b))}{\partial x^i} \\
 &= Q^{ij}(t) \frac{\partial a^j(x^m, t)}{\partial x^k} \frac{\partial(Q^{nk}(t^* - b)(x^{*n} - c^n(t^* - b)))}{\partial x^{*i}} \\
 &= \frac{\partial a^j(x^m, t)}{\partial x^k} Q^{ij}(t) Q^{ik}(t) = \frac{\partial a^j(x^m, t)}{\partial x^j} = \text{div} \mathbf{a}
 \end{aligned}$$

But the material derivative of objective vector $\dot{\mathbf{a}}$ is not objective: From (3.56), using (3.28), it follows

$$\begin{aligned}
 (\dot{a}^i)^* &\equiv \frac{\partial a^i(X^J, t^*)}{\partial t^*} = \frac{\partial(Q^{ij}(t^* - b)a^j(X^K, t^* - b))}{\partial t^*} \\
 &= Q^{ij}(t) \frac{\partial a^j(X^K, t)}{\partial t} \frac{d(t^* - b)}{dt^*} \\
 &\quad + \frac{dQ^{ij}(t)}{dt} \frac{d(t^* - b)}{dt^*} a^j(X^K, t) = Q^{ij} \dot{a}^j + \dot{Q}^{ij} a^j
 \end{aligned}$$

and therefore $\dot{\mathbf{a}}$ is not an objective vector.

Transformation (frame change) of objective (second order) tensor (3.57) gives the objectivity of the scalars $\text{tr} \mathbf{A}$ and $\det \mathbf{A}$:

$$(\text{tr} \mathbf{A})^* = \text{tr} \mathbf{A}^* = A^{*ii} = Q^{ik} A^{kl} Q^{il} = \delta^{kl} A^{kl} = A^{ll} = \text{tr} \mathbf{A}$$

$$(\det \mathbf{A})^* = \det \mathbf{A}^* = \det \mathbf{Q} \mathbf{A} \mathbf{Q}^T = \det \mathbf{Q} \det \mathbf{A} \det \mathbf{Q}^T = \det \mathbf{Q} \mathbf{Q}^T \det \mathbf{A} = \det \mathbf{A}$$

Also the vector $\text{div} \mathbf{A}$ is objective (from (3.57)) using

$$\begin{aligned}
 (\text{div} \mathbf{A})^* &\equiv \frac{\partial A^{*ij}(x^*, t^*)}{\partial x^{*j}} = \frac{\partial Q^{ik}(t) A^{kl}(x^n, t) Q^{jl}(t)}{\partial x^{*j}} \\
 &= \frac{\partial(Q^{ik}(t^* - b) A^{kl}(Q^{pn}(t^* - b)(x^{*p} - c^p(t^* - b)), t^* - b) Q^{jl}(t^* - b))}{\partial x^{*j}} \\
 &= Q^{ik}(t) \frac{\partial A^{kl}(Q^{pn}(t^* - b)(x^{*p} - c^p(t^* - b)), t^* - b)}{\partial x^{*j}} Q^{jl}(t)
 \end{aligned}$$

$$\begin{aligned}
 &= Q^{ik}(t) \frac{\partial A^{kl}(x^m, t)}{\partial x^q} \frac{\partial Q^{pq}(t^* - b)(x^{*P} - c^P(t^* - b))}{\partial x^{*j}} Q^{jl}(t) \\
 &= Q^{ik}(t) \frac{\partial A^{kl}(x^m, t)}{\partial x^q} Q^{jq}(t) Q^{jl}(t) = Q^{ik}(t) \frac{\partial A^{kl}(x^m, t)}{\partial x^l} = Q^{ik}(\operatorname{div} \mathbf{A})^k
 \end{aligned}$$

Therefore, $\operatorname{div} \mathbf{A}$ of objective tensor \mathbf{A} is an objective vector. Q.E.D.

As we noted in the precepts above the remaining relations of Sect. 3.1 are also valid in all frames, e.g., (3.21), (3.22) or Reynolds theorem (3.24). Because of no influence of the change of frame on the reference configuration (and material points), no such influence may be also expected on material volume \mathcal{V} , material surface $\partial \mathcal{V}$ (they behave as objective scalars), and the outside normal \mathbf{n} should be an objective vector.¹²

Objectivity of other quantities occurring in the remaining chapters may be obtained analogically.

Summary. The change of frame refers to the change (rotation, translation, etc.) of coordinate system used to describe space and time variations and the effects of this change on various (physical) quantities or functions. The change is mathematically described by (3.25) and (3.26). Special quantities which are in some sense invariant to this change were called objective or frame-indifferent, cf. (3.30)–(3.32), and are of special importance for the methodology of rational thermodynamics. The objectivity of several quantities or functions was tested; the most important conclusions are the objectivity of stretching tensor, cf. (3.54), and the nonobjectivity of velocity, cf. (3.35), and its gradient, cf. (3.52), and of deformation gradient, cf. (3.49).

¹² Moreover, it should be expected that

$$\left(\int_{\mathcal{V}} \psi \, dv \right)^* = \int_{\mathcal{V}} \psi^* \, dv, \quad \left(\int_{\partial \mathcal{V}} \psi \mathbf{n} \, da \right)^* = \int_{\partial \mathcal{V}} \psi^* \mathbf{Q} \mathbf{n} \, da$$

because the objectivity of da , dv follows from the objectivity of space intervals (ψ may even be a component of a vector or a tensor).

Note also that the following relationships are valid in the starred frame for the time derivative of function $\varphi(t)$ (see (3.26), (3.28))

$$\overset{*}{\dot{\varphi}} \equiv \frac{d\varphi^*(t^*)}{dt^*} = \frac{d\varphi^*(t^*)}{dt} \frac{d(t^* - b)}{dt^*} = \frac{d\varphi^*(t^*)}{dt} = \dot{\varphi}^*$$

Such a function φ may be, e.g., $\psi(\mathbf{X}, t)$ or $\Psi(t)$ in (3.21); for the latter the relation (3.22) and the previous formula (with (3.50)) gives

$$\left(\int_{\mathcal{V}} \dot{\psi} \, dv \right)^* = \int_{\mathcal{V}_0} (\dot{\psi} J)^* \, dV = \int_{\mathcal{V}_0} \dot{\psi}^* J^* \, dV = \int_{\mathcal{V}} \dot{\psi}^* \, dv$$

because \mathcal{V}_0 is a material volume in reference configuration.

3.3 Balances of Mass, Momentum, and Moment of Momentum

In this and in the following paragraphs, we formulate general postulates, mostly balances for a single substance [6–9, 11, 13, 23]. We use classical mechanics and formulate them in the inertial frame (specifically those fixed with distant, remote stars, see Sect. 3.2); generalization in other frames (even noninertial) will be shown at the end of the discussion of each special balance (for further developments, see end of Sect. 3.4).

To formulate the *balance of mass* let us consider the single (one-constituent) body in arbitrary actual configuration (in inertial frame noted above).

As a primitive we assign to each particle \mathbf{X} of this body the (*mass density*) ρ —positive and (assuming) objective (frame indifferent) scalar. *Mass* of the body or its arbitrary part with material volume \mathcal{V} is then

$$\int_{\mathcal{V}} \rho \, dv \quad (3.58)$$

It follows that mass is continuous and additive with volume (cf. Rem. 7) and therefore we exclude the concentrated masses (mass points) from consideration. The *mass balance* is postulated by the conservation of mass of some part of the body (or body itself) containing the same particles during its motion. In other words, the mass of material volume \mathcal{V} is not changed in time

$$\frac{d}{dt} \int_{\mathcal{V}} \rho \, dv = 0 \quad (3.59)$$

Using Reynolds theorem (3.24), mass balance (3.59) may be written in (space) fixed volume V with surface ∂V as

$$\frac{d}{dt} \int_V \rho \, dv + \int_{\partial V} \rho \mathbf{v} \cdot \mathbf{n} \, da = 0 \quad (3.60)$$

i.e., mass in the fixed volume may be changed only by a flow through its (fixed) boundary. Using Gauss theorem (3.23) in (3.60) we have

$$\int_V \frac{\partial \rho}{\partial t} \, dv + \int_V \operatorname{div}(\rho \mathbf{v}) \, dv = 0 \quad (3.61)$$

We assume now validity of this mass balance for any part of the body, specifically for that whose volume V is sufficiently small. Then also the integrand here must be zero and we obtain the *local mass balance*

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \rho \mathbf{v} = 0 \quad (3.62)$$

Another form of local mass balance follows using material derivative (3.8) of the density

$$\dot{\rho} + \rho \operatorname{div} \mathbf{v} = 0 \quad (3.63)$$

We note that using Euler relation (3.17) we can write the mass balance (3.63) as

$$\frac{\dot{\rho}}{\rho J} = 0 \quad (3.64)$$

which after time integration gives the mass balance in the form

$$\rho_0 = \rho J \quad (3.65)$$

Here ρ_0 is the density in the reference configuration (because $J = 1$ when $\mathbf{F} = \mathbf{1}$).

Assumed continuity and additivity of mass permits to introduce (cf. Rem. 7) the specific quantities φ related with densities ψ by

$$\psi = \rho \varphi \quad (3.66)$$

We note two useful formulae for specific quantities φ (which may also be a component of vector or tensor)

$$\frac{\partial \rho \varphi}{\partial t} + \operatorname{div} \rho \varphi \mathbf{v} = \rho \dot{\varphi} \quad (3.67)$$

$$\frac{d}{dt} \int_{\mathcal{V}} \rho \varphi \, dv = \int_{\mathcal{V}} \rho \dot{\varphi} \, dv \quad (3.68)$$

which follows for (3.66) from (3.22), (3.63) in material volume \mathcal{V} .

Mass balances obtained so far were formulated and deduced in an inertial frame fixed with distant stars. But their form is the same in any frame (even a noninertial one), i.e., formulae (3.58)–(3.68) are independent of the frame. This may be seen from the assumption of objectivity of scalar mass density ρ ((3.30) is valid). Using the last formulae from Rem. 12 with objective density ρ as the scalar ψ we find general validity of mass balance (3.59) in any frame. In some new frame, Reynolds theorem (3.24) may be quite analogously deduced and used and then, by localization, all remaining formulae (3.60)–(3.68) are valid in any frame. Indeed, e.g., (3.63) is valid in any frame because of the objectivity of the material derivative of the objective scalar $\dot{\rho}$ and, see (3.16) $\operatorname{div} \mathbf{v} = \operatorname{tr} \mathbf{D}$, because the trace of objective tensor (3.54) is objective. Similarly, so is (3.65) with the same ρ_0 (reference is unique for all actual configurations) and by (3.50). This is also (3.68) for φ from such a new frame.

To postulate the *balance of momentum*, we define the *momentum* or *linear momentum* of a part of body (or the whole body) with material volume \mathcal{V} in actual configuration in given (arbitrary) frame as

$$\int_{\mathcal{V}} \rho \mathbf{v} \, dv \quad (3.69)$$

The postulate of the *balance of momentum* expresses the experience that the time change of momentum (3.69) is equal to the *forces* acting on the corresponding part of body with material volume \mathcal{V} in actual configuration. Simple, classical formulation of this balance is done in an inertial frame, specifically that fixed with distant stars. The main reason for this is the nonobjectivity of velocity in (3.69), see (3.38); forces are a priori considered as objective. Below (3.78) we show that such formulation is the same in any inertial frame and that in a general frame the balance must be modified a little.

Forces are primitive quantities and we confine here two types of forces: the *external* or *body, volume, outer* forces exist inside material volume \mathcal{V} but have their origin outside the (whole) body and are characterized by a vector of *body, or volume* forces \mathbf{b} per mass unit (an example is the gravitation coming from the environment of the body). The second type are the *contact* or *surface* forces acting on the surface of the chosen part of the body. These imaginable forces come from the outside neighborhood of the surface considered (“short range interaction forces” from the outside part of the same body) and they are characterized by the *stress vector* or *traction* \mathbf{t} —force per unit surface of the chosen part coming from its outside.¹³ Therefore, we exclude in the following a “long range interaction body forces” among distant parts of the same body like self-gravitation; for such a more general case see e.g., [18, 19, 30]. They might appear in ion mixtures, but in salt solution may be neglected by electroneutrality, cf. Rems. 6 and 32 in Chap. 4.

The *Balance of momentum* or *balance of linear momentum* for an arbitrary part of a body in actual configuration and in inertial frame (fixed on distant stars) is postulated as¹⁴

$$\frac{d}{dt} \int_{\mathcal{V}} \rho \mathbf{v} dv = \int_{\partial \mathcal{V}} \mathbf{t} da + \int_{\mathcal{V}} \rho \mathbf{b} dv \quad (3.70)$$

where this part of the body has the material volume \mathcal{V} with the material surface $\partial \mathcal{V}$. We shall assume in the following, that vectors \mathbf{t} , \mathbf{b} are objective (frame indifferent).

Experience shows that the body force is a field (i.e., a function of position \mathbf{x} and time t) but that traction depends not only on the \mathbf{x} and t but also on the orientation of the surface; this is expressed by *Cauchy's postulate*¹⁵

¹³ On the real surface of the whole body the surface forces \mathbf{t} (originated from the outside of the whole body) are given by boundary conditions; cf. Rems. 18 and 24 in this chapter, 9 in Chap. 1.

¹⁴ Again [7, 10, 18–20] as we noted in Rem. 7, it would be more natural to postulate forces for any part of volume or surface (which bound them) and then to deduce $\rho \mathbf{b}$ or \mathbf{t} as the volume or surface densities.

In fact, the formulation of balances in Sects. 3.3 and 3.4 for each part of the body is motivated by the *solidification principle*: we imagine the part of the body isolated from the remainder of the body and interactions with this remainder and surroundings of the body are expressed by appropriate (volume or surface) densities. This principle will be used also in the following, e.g., contact and body forces in formulation of (3.70) are such interactions.

¹⁵ E.g., hydrostatic pressure (typical traction in steady fluid) is directed always perpendicularly to any orientation of the surface in a given place. Moreover, assumption (3.71) may be also proved

$$\mathbf{t} = \mathbf{t}(\mathbf{x}, t, \mathbf{n}) \tag{3.71}$$

where \mathbf{n} is the outside normal to the surface $\partial\mathcal{V}$ in a given place \mathbf{x} and instant t .

In fact, the dependence of \mathbf{t} on \mathbf{n} (3.71) is linear as the *Cauchy theorem* asserts

$$\mathbf{t} = \mathbf{T}\mathbf{n} \tag{3.72}$$

where the field $\mathbf{T} = \mathbf{T}(\mathbf{x}, t)$ is the *stress tensor*.

The Cauchy theorem may be proved by application of (3.70) to an infinitesimal tetrahedron at considered place \mathbf{x} and instant t , the walls of which are formed by coordinate planes and a tangent plane perpendicular to considered \mathbf{n} . The estimate of the surface and volume integrals in (3.70) gives (using (3.68))

$$\rho \dot{v} \Delta v = \mathbf{t} \Delta a + \mathbf{t}_j \Delta a^j + \rho \mathbf{b} \Delta v \tag{3.73}$$

Here Δv is the volume of the tetrahedron and \mathbf{t} and \mathbf{t}_j are the tractions on the surfaces Δa and Δa^j (the latter are formed by coordinate axes) respectively (summation rule is assumed). But $\Delta v = (1/3)h \Delta a$ (where h is the height of the tetrahedron) and $\Delta a^j = n^j \Delta a$ where n^j are components of \mathbf{n} . Inserting these relations into (3.73) and limiting $h \rightarrow 0$ (assuming continuity) we obtain $\mathbf{t} = -\mathbf{t}_j \mathbf{n}^j$ which is (3.72) in Cartesian components $t^i = T^{ij} n^j$ if we take T^{ij} as i th component of vector $-\mathbf{t}_j$. Moreover, \mathbf{T} depends only on \mathbf{x} and t because also \mathbf{t}_j depends on \mathbf{x} and t and not on \mathbf{n} as follows from the construction of the tetrahedron. The sign of \mathbf{T} is given by a convention which gives to \mathbf{t} the meaning of tension by which the exterior of the surface $\partial\mathcal{V}$ acts on material inside (cf. e.g. [13]; modern versions of this proof [7, 30–32] show the much more general validity of (3.72)). The stress tensor \mathbf{T} is objective because of the objectivity of \mathbf{t} and (arbitrary) \mathbf{n} (see end of Sect. 3.2); the deduction is similar to that of (3.32).

Inserting (3.72) into (3.70) we obtain the balance of momentum in the inertial frame (fixed on distant stars) as

$$\overline{\int_{\mathcal{V}} \rho \mathbf{v} dv} = \int_{\partial\mathcal{V}} \mathbf{T}\mathbf{n} da + \int_{\mathcal{V}} \rho \mathbf{b} dv \tag{3.74}$$

$$\frac{d}{dt} \int_{\mathcal{V}} \rho \mathbf{v} dv + \int_{\partial\mathcal{V}} \rho \mathbf{v}(\mathbf{v} \cdot \mathbf{n}) da = \int_{\partial\mathcal{V}} \mathbf{T}\mathbf{n} da + \int_{\mathcal{V}} \rho \mathbf{b} dv \tag{3.75}$$

where the last form (3.75) was obtained using (3.24) (Reynolds theorem obtainable in any frame) for the volume V with the surface ∂V fixed in the space. Because (3.74) and (3.75) are valid for any volume we can use the Gauss theorem to convert the surface integrals into those of volume (only those are permitted by stress field

(Footnote 15 continued)

[7, 21, 30, 31]; from this proof it follows that \mathbf{t} cannot depend on the other local properties of surface, like curvature, etc.

as distinct from traction (3.71)) and using (3.68) we obtain the local balances of momentum in the inertial frame

$$\rho \dot{\mathbf{v}} = \operatorname{div} \mathbf{T} + \rho \mathbf{b} \quad (3.76)$$

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v}) = \operatorname{div} \mathbf{T} + \rho \mathbf{b} \quad (3.77)$$

(in components $(\operatorname{div} \mathbf{T})^i = \partial T^{ij} / \partial x^j$ and $(\operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v}))^i = \partial \rho v^i v^j / \partial x^j$).

So far we have assumed that the inertial frame (fixed with distant stars) was used. To transform balances (3.70), (3.74)–(3.77) into another frame we note that the stress tensor \mathbf{T} is objective (see below (3.72)). Considering any new (starred) frame and using (3.30)–(3.32), (3.44), (3.46) (note that $\operatorname{div} \mathbf{T}$ is objective vector and ρ objective scalar) in (3.76) (multiplied by orthogonal transformation \mathbf{Q} of coordinates in the inertial frame to the new one at considered instant) we obtain the *local balance of momentum* in any frame (stars denoting the new frame were removed)

$$\rho \dot{\mathbf{v}} = \operatorname{div} \mathbf{T} + \rho(\mathbf{b} + \mathbf{i}) \quad (3.78)$$

where the inertial acceleration \mathbf{i} (3.46) in this new frame is

$$\mathbf{i} = 2\dot{\underline{\Omega}}(\mathbf{v} - \dot{\mathbf{c}}) - \underline{\Omega}^2(\mathbf{x} - \mathbf{c}) + \dot{\underline{\Omega}}(\mathbf{x} - \mathbf{c}) + \ddot{\mathbf{c}} \quad (3.79)$$

Here, the tensor $\underline{\Omega}$ is the angular velocity (of original, inertial frame relative to new one) (3.39) and \mathbf{c} is the position of origin, \mathbf{v} is the velocity, \mathbf{x} the position in the new frame at the considered instant.

Then it is not difficult to see that transformation of any momentum balance (3.70), (3.74)–(3.77) into an arbitrary frame means inserting $\mathbf{b} + \mathbf{i}$ instead of \mathbf{b} . Indeed, the starting postulate of momentum balance (3.70) has in an arbitrary new frame the form

$$\overline{\int_{\mathcal{V}} \rho \mathbf{v} dv} = \int_{\partial \mathcal{V}} \mathbf{t} da + \int_{\mathcal{V}} \rho(\mathbf{b} + \mathbf{i}) dv \quad (3.80)$$

because balance (3.78) in the new frame may be integrated in this frame through material volume (which is independent of the frame, cf. end of Sect. 3.2) and uses Gauss theorem (3.23), (3.72) and (3.68) (where φ is component of velocity) in the new frame (because these formulae are the same in all frames as well as the Reynolds theorem (3.24), mass balances above, etc.).

Repeating the previous procedure in the new frame we obtain all remaining balances in this new arbitrary frame, e.g.,

$$\overline{\int_{\mathcal{V}} \rho \mathbf{v} dv} = \int_{\mathcal{V}} \rho \dot{\mathbf{v}} dv = \int_{\partial \mathcal{V}} \mathbf{T} \mathbf{n} da + \int_{\mathcal{V}} \rho(\mathbf{b} + \mathbf{i}) dv \quad (3.81)$$

$$\frac{d}{dt} \int_V \rho \mathbf{v} dv + \int_{\partial V} \rho \mathbf{v} (\mathbf{v} \cdot \mathbf{n}) da = \int_{\partial V} \mathbf{T} \mathbf{n} da + \int_V \rho (\mathbf{b} + \mathbf{i}) dv \quad (3.82)$$

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v}) = \operatorname{div} \mathbf{T} + \rho (\mathbf{b} + \mathbf{i}) \quad (3.83)$$

Because of zero inertial acceleration (3.48), we can see from these general results (3.78)–(3.83), that the balances (3.70), (3.74)–(3.77) are valid in any inertial frame and not only in the one fixed with the distant stars. This assertion expresses the Galilean relativity principle about the impossibility of preference of any inertial frame.

Momentum balances (3.81), and (3.78) in the arbitrary frame may be written as (cf. [1, 7, 18–20, 22, 33])

$$\mathbf{o} = \int_{\partial V} \mathbf{T} \mathbf{n} da + \int_V \rho \underline{\beta} dv \quad (3.84)$$

$$\mathbf{o} = \operatorname{div} \mathbf{T} + \rho \underline{\beta} \quad (3.85)$$

where the *total body force* $\underline{\beta}$ (coming from the outside of the body) is defined by

$$\underline{\beta} \equiv \mathbf{b} + \mathbf{i} - \dot{\mathbf{v}} \quad (3.86)$$

This force $\underline{\beta}$ is objective: indeed, (3.85) is valid in all frames, therefore

$$\underline{\beta}^* = (-(1/\rho) \operatorname{div} \mathbf{T})^* = (-(1/\rho^*) (\operatorname{div} \mathbf{T})^*) = \mathbf{Q} (-(1/\rho) \operatorname{div} \mathbf{T}) = \mathbf{Q} \underline{\beta} \quad (3.87)$$

where objectivity of scalar ρ and vector $\operatorname{div} \mathbf{T}$ have been used (see Sect. 3.2; stress tensor \mathbf{T} is objective).

Balance of momentum in the objective form (3.84), (3.85) may be interpreted as the general action and reaction law: sum of all forces is zero (in total body force (3.86) the force $\mathbf{i} - \dot{\mathbf{v}}$ caused by “distant, remote stars” is included).

To formulate another main principle—the balance of moment of momentum—we introduce for some part of body (or body itself) with material volume \mathcal{V} in actual configuration of the considered frame the *moment of momentum* or *angular momentum* related to the point \mathbf{y} as follows¹⁶

¹⁶ We use the outer product \wedge defined for two vectors \mathbf{a} , \mathbf{b} as $\mathbf{a} \wedge \mathbf{b} \equiv \mathbf{a} \otimes \mathbf{b} - \mathbf{b} \otimes \mathbf{a}$, i.e. $(\mathbf{a} \wedge \mathbf{b})^{ij} = a^i b^j - a^j b^i$. This product is obviously the skew-symmetric tensor which, using the results from Rem. 10, is equivalent to the axial vector created by the vector product of these vectors, see Rem. 6

$$\mathbf{b} \times \mathbf{a} = -\mathbf{a} \times \mathbf{b}$$

Then, e.g., the balance of angular momentum (3.90) may be written in a more traditional way as

$$\int_{\mathcal{V}} (\mathbf{x} - \mathbf{y}) \times \rho \dot{\mathbf{v}} dv = \int_{\partial \mathcal{V}} (\mathbf{x} - \mathbf{y}) \times \mathbf{T} \mathbf{n} da + \int_{\mathcal{V}} (\mathbf{x} - \mathbf{y}) \times \rho \mathbf{b} dv$$

$$\int_{\partial\mathcal{V}} (\mathbf{x} - \mathbf{y}) \wedge \rho \mathbf{v} \, dv \quad (3.88)$$

Here, \mathbf{x} is the place where density ρ and \mathbf{v} is considered and \mathbf{y} is the point which may be outside of the body and usually fixed in the considered frame.

To obtain a simple form of the balance of moment of momentum, we confine its formulation to inertial frame with angular moment (3.88) having point \mathbf{y} fixed here (although we use here the inertial frame fixed with distant stars, resulting formulations are valid in any inertial frame as will be shown at the end of this section). Again, the main reason for that is the nonobjectivity of \mathbf{x} , \mathbf{y} , \mathbf{v} in (3.88), cf. (3.25), (3.38); generalization of this balance in the arbitrary frame will be discussed below but we note that the main local result—symmetry of stress tensor (3.93) below—is valid in the arbitrary frame.

Such a balance of the moment of momentum (balance of angular moment) asserts that the time change of the moment of momentum is equal to *torques* acting on a considered part of the body (or the body itself). Here we confine to the simplest case of (mechanically) nonpolar materials where torques are moments of forces (i.e., their outer products of Rem. 16 with $\mathbf{x} - \mathbf{y}$) used in the preceding balance of momentum.¹⁷

Therefore, the *balance of moment of momentum* or *balance of angular momentum* related to the fixed point \mathbf{y} in actual configuration in the inertial frame (fixed with distant stars) for (arbitrary part of) body with material volume \mathcal{V} and its surface $\partial\mathcal{V}$ is postulated as

$$\frac{d}{dt} \int_{\mathcal{V}} (\mathbf{x} - \mathbf{y}) \wedge \rho \mathbf{v} \, dv = \int_{\partial\mathcal{V}} (\mathbf{x} - \mathbf{y}) \wedge \mathbf{T} \mathbf{n} \, da + \int_{\mathcal{V}} (\mathbf{x} - \mathbf{y}) \wedge \rho \mathbf{b} \, dv \quad (3.89)$$

Traction \mathbf{t} is here expressed through the stress tensor by (3.72). We also note that postulating (3.89) for one fixed point \mathbf{y} the form (3.89) is valid for arbitrary but fixed point (say \mathbf{y}_0 as follows from the balance of linear momentum (3.74) multiplied by constant $(\mathbf{y} - \mathbf{y}_0) \wedge$ (i.e., as outer product in Rem. 16) and by summation with (3.89), of course all in our inertial frame). For this reason the origin $\mathbf{y} = \mathbf{o}$ is often used in formulations of this postulate, e.g., [16], without loss of generality.

Using (3.68), (3.7) (namely $\dot{\mathbf{x}} \wedge \mathbf{v} = \mathbf{o}$) and the assumption of fixed point, i.e., the time derivative $\dot{\mathbf{y}} = \mathbf{o}$ (note that (3.25) applied on point \mathbf{y} shows that \mathbf{y} may be at most a function of time in the arbitrary frame; cf. below (3.94)), we obtain

¹⁷ In more general (mechanically) *polar* materials [13, 34], the local result (3.93) must be changed (cf. also Rems. 32 in this chapter, 9 in Chap. 4). Namely, the balance (3.89) then contains (besides moments of forces) *torques* expressing the direct exchange of angular moment on a microscopic level (something like heat in energy exchange). These “microscopic” torques may be expressed by the objective field of density of skew-symmetric tensor \mathbf{M} adding to the right-hand side of the postulate (3.89) the integral $\int_{\mathcal{V}} \mathbf{M} \, dv$. Then instead of local result (3.93), we obtain

$$\mathbf{T} - \mathbf{T}^T = \mathbf{M}.$$

$$\int_{\mathcal{V}} (\mathbf{x} - \mathbf{y}) \wedge \rho \dot{\mathbf{v}} \, dv = \int_{\partial \mathcal{V}} (\mathbf{x} - \mathbf{y}) \wedge \mathbf{T} \mathbf{n} \, da + \int_{\mathcal{V}} (\mathbf{x} - \mathbf{y}) \wedge \rho \mathbf{b} \, dv \quad (3.90)$$

Using Gauss' theorem (cf. (3.23); note that the following skew-symmetric tensor is in components $(\operatorname{div}((\mathbf{x} - \mathbf{y}) \wedge \mathbf{T}))^{ij} = \partial((x^i - y^i)T^{jk} - (x^j - y^j)T^{ik})/\partial(x^k)$, cf. Rem. 16) and by localization using assumed validity of (3.90) for any \mathcal{V} , we obtain

$$(\mathbf{x} - \mathbf{y}) \wedge \rho \dot{\mathbf{v}} = \operatorname{div}((\mathbf{x} - \mathbf{y}) \wedge \mathbf{T}) + (\mathbf{x} - \mathbf{y}) \wedge \rho \mathbf{b} \quad (3.91)$$

Calculating divergence (simply in component form above, \mathbf{y} is fixed) we obtain

$$\operatorname{div}((\mathbf{x} - \mathbf{y}) \wedge \mathbf{T}) = \mathbf{T}^T - \mathbf{T} + (\mathbf{x} - \mathbf{y}) \wedge \operatorname{div} \mathbf{T} \quad (3.92)$$

Inserting it in (3.91) and using in this inertial reference configuration the balance of momentum (3.76) multiplied by $(\mathbf{x} - \mathbf{y}) \wedge$ from the left, we obtain the *local balance of moment of momentum* as

$$\mathbf{T} = \mathbf{T}^T \quad (3.93)$$

expressing the symmetry of the stress tensor (but see Rem. 17). Though our deduction was performed in the inertial frame fixed with distant stars, we can see that such symmetry of the stress tensor is valid in any frame, even a noninertial one, because the stress \mathbf{T} is an objective tensor (see above and (3.32)).

Starting with (3.93) in any frame and tracing back the deduction we can obtain the integral form of the balance of angular momentum even in the noninertial frame; as may be expected such a result will be more complicated because of the nonobjectivity of \mathbf{x} , \mathbf{y} , \mathbf{v} and objectivity of forces \mathbf{T} , \mathbf{b} , cf. e.g. [7, 14].

Namely, taking the outer product of $\mathbf{x} - \mathbf{y}$ with local momentum balance (3.78) in an arbitrary, even noninertial frame we have (we use (3.92) and the validity of moment of momentum balance (3.93) in any frame)

$$(\mathbf{x} - \mathbf{y}) \wedge \rho \dot{\mathbf{v}} = \operatorname{div}((\mathbf{x} - \mathbf{y}) \wedge \mathbf{T}) + (\mathbf{x} - \mathbf{y}) \wedge \rho (\mathbf{b} + \mathbf{i}) \quad (3.94)$$

where \mathbf{y} may be an arbitrary function of time (at most, cf. our remark above (3.90); it would be better to denote all quantities in this new arbitrary frame say by stars as in Sect. 3.2, e.g. \mathbf{y}^* may be obtained from \mathbf{y} by (3.25) as $\mathbf{y}^* = \mathbf{c}(t) + \mathbf{Q}(t)\mathbf{y}$ with fixed \mathbf{y} (say from inertial frame fixed with distant stars above), but we do not use this mark for simplicity).

Integrating (3.94) through material volume \mathcal{V} in this new arbitrary “starred” frame and using Gauss' theorem (3.23) we obtain (3.90) with $\mathbf{b} + \mathbf{i}$ instead of \mathbf{b} . Because $\overline{(\mathbf{x} - \mathbf{y}) \wedge \mathbf{v}} = (\mathbf{x} - \mathbf{y}) \wedge \dot{\mathbf{v}} - \dot{\mathbf{y}} \wedge \mathbf{v}$ (namely $\dot{\mathbf{x}} \wedge \mathbf{v} = \mathbf{v} \wedge \mathbf{v} = \mathbf{0}$; scalar ρ is objective) we obtain by (3.68) (\mathbf{y} is function of time at most) the balance of the moment of momentum related to even the nonfixed point \mathbf{y} in an arbitrary (even noninertial) frame as

$$\overline{\int_{\mathcal{V}} (\mathbf{x} - \mathbf{y}) \wedge \rho \mathbf{v} \, dv} + \dot{\mathbf{y}} \wedge \int_{\mathcal{V}} \rho \mathbf{v} \, dv = \int_{\partial \mathcal{V}} (\mathbf{x} - \mathbf{y}) \wedge \mathbf{T} \mathbf{n} \, da + \int_{\mathcal{V}} (\mathbf{x} - \mathbf{y}) \wedge \rho (\mathbf{b} + \mathbf{i}) \, dv \quad (3.95)$$

Using here the Reynolds theorem (3.24) we can, e.g., write the balance of moment of momentum related to even a nonfixed point \mathbf{y} in an arbitrary (even noninertial) frame for a fixed volume V in actual configuration as

$$\begin{aligned} \frac{d}{dt} \int_V (\mathbf{x} - \mathbf{y}) \wedge \rho \mathbf{v} \, dv + \int_{\partial V} (\mathbf{x} - \mathbf{y}) \wedge \rho \mathbf{v} (\mathbf{v} \cdot \mathbf{n}) \, da + \dot{\mathbf{y}} \wedge \int_V \rho \mathbf{v} \, dv \\ = \int_{\partial V} (\mathbf{x} - \mathbf{y}) \wedge \mathbf{T} \mathbf{n} \, da + \int_V (\mathbf{x} - \mathbf{y}) \wedge \rho (\mathbf{b} + \mathbf{i}) \, dv \end{aligned} \quad (3.96)$$

Therefore, as follows from (3.95), if point \mathbf{y} is fixed (i.e., $\dot{\mathbf{y}} = \mathbf{o}$) the balances of moment of momentum (3.89) may be used also in an arbitrary (even noninertial) frame if body force \mathbf{b} is enlarged by inertial acceleration \mathbf{i} (3.79) (i.e., \mathbf{b} is substituted by $\mathbf{b} + \mathbf{i}$). This is valid also for balance (3.90) (see deduction of (3.95)) and for local balance (3.91) (cf. (3.94)).

Balance of moment of momentum (3.93) expressed through the symmetry of a stress tensor (at least for mechanically nonpolar materials, cf. Rem. 17) is valid in any frame, even noninertial. Finally we can see that because (3.48) is valid for transformations between any inertial frames, the balances of angular momentum related to fixed \mathbf{y} (3.89)–(3.91) are valid in any inertial frame and not only in those fixed with distant stars.

Summary. The first three balance equations are formulated in this section. The balances are necessary conditions to be fulfilled not only in thermodynamics but generally (in continuum mechanics). The balance of mass was formulated locally in several alternatives—(3.62), (3.63), or (3.65). The most important consequence of the balance of momentum is the Cauchy theorem (3.72), which introduces the stress tensor. The local form of this balance is then expressed by (3.76) or (3.77). The most relevant outcome of the balance of moment of momentum is the symmetry of the stress tensor (3.93). Note that in this section also an important class of quantities—the specific quantities—was introduced by (3.66); note particularly their derivative properties (3.67) and (3.68).

3.4 Energy Balance and Entropy Inequality

In Chap. 1 we postulate the First Law as (1.3) which gives the existence of internal energy fulfilling (1.5). Similarly as in Sect. 2.1 we can write (1.5) as a balance: the time derivative of internal energy is equal to the sum of heating and power (cf. (2.1)) [11, 18, 22, 35]. This is applicable to the material volume of a (nonuniform) body or its arbitrary part consisting of a single substance. We postulate the existence of a

specific internal energy u and assume that heating is composed of the *surface heating* q (exchange of heat between neighbourhood parts by conductivity) and the *volume heating* Q (exchange of heat by radiation from the outside of the body) which are surface and volume densities respectively.¹⁸ Therefore assuming that power is given by forces from Sect. 3.3, i.e., by traction \mathbf{t} (3.72) with symmetrical stress \mathbf{T} (3.93) and the total body force $\underline{\beta}$ (3.86), we can postulate the *balance of energy* in the form

$$\overline{\int_{\mathcal{V}} \rho u \, dv} = \int_{\partial\mathcal{V}} q \, da + \int_{\mathcal{V}} Q \, dv + \int_{\partial\mathcal{V}} \mathbf{v} \cdot \mathbf{Tn} \, da + \int_{\mathcal{V}} \rho \underline{\beta} \cdot \mathbf{v} \, dv \quad (3.97)$$

for any material volume \mathcal{V} with the surface $\partial\mathcal{V}$ but in actual configuration, cf. end of Sect. 3.1. The justification of the name *internal energy* on the left hand side follows from using all forces (including those inertial in $\underline{\beta}$) for the construction of power on the right-hand side, cf. discussion of (1.5).

We postulate also that u , q and Q are objective scalars (but see Rem. 21); then (3.97) is valid in all frames: by Rem. 12 the first three integrals in (3.97) are objective as well as the remaining scalar

$$\int_{\partial\mathcal{V}} \mathbf{v} \cdot \mathbf{Tn} \, da + \int_{\mathcal{V}} \rho \underline{\beta} \cdot \mathbf{v} \, dv = \int_{\mathcal{V}} (\mathbf{v} \cdot (\operatorname{div} \mathbf{T} + \rho \underline{\beta}) + \operatorname{tr}(\mathbf{L}\mathbf{T})) \, dv = \int_{\mathcal{V}} \operatorname{tr}(\mathbf{D}\mathbf{T}) \, dv \quad (3.98)$$

obtained by (3.23), (3.14), (3.85), (3.15), (3.93). Its objectivity follows from the objectivity of \mathbf{D} , \mathbf{T} and therefore of $\mathbf{D}\mathbf{T}$ (as may be easily seen) and its trace, see Sects. 3.2 and 3.3.

Densities in (3.97) are field quantities; but¹⁹ we assume that the heating surface density q depends, in excess, on the external normal \mathbf{n}

$$q = q(\mathbf{x}, t, \mathbf{n}) \quad (3.99)$$

Then using the tetrahedron arguments (similarly as in deduction of (3.72)) we prove from (3.99), (3.97), that dependence on \mathbf{n} is linear

$$q = -\mathbf{q} \cdot \mathbf{n} \quad (3.100)$$

¹⁸ Exchange of radiation between distant parts of the same body is neglected; q on the real surface of body is given as a boundary condition. Assuming the validity of such a balance for each part of the body, we use again the principle of solidification and again volume and surface densities (ρu , Q , q etc.) could be deduced from more plausible primitives. Cf. Rems. 7, 13 and 14.

¹⁹ Surface heating is scalar. Vectorial heat flux in (3.100) will be deduced quite similarly as the stress tensor was obtained from the traction in (3.72). Dependence of q on \mathbf{n} may be expected, e.g., in a body under temperature gradient it may be expected in a given place that q on the surface perpendicular to such a gradient will be greater then on the surface parallel to it.

i.e., there exists a field²⁰ of the *heat flux* vector $\mathbf{q} = \mathbf{q}(\mathbf{x}, t)$. Indeed, if we apply (3.97) to a small tetrahedron (as in (3.73)) and use (3.68) and Gauss' theorem, we obtain

$$\rho \dot{u} \Delta v = q \Delta a + q^j \Delta a^j + Q \Delta v + (\operatorname{div}(\mathbf{v}\mathbf{T})) \Delta v + \rho \underline{\beta} \cdot \mathbf{v} \Delta v \quad (3.101)$$

Here $\Delta v = (1/3)h \Delta a$, h , Δa , $\Delta a^j = n^j \Delta a$ have the same meaning as in (3.73). Inserting these relations into (3.101) and limiting $h \rightarrow 0$ we obtain $q = -q^j n^j$ where q^j (independent of \mathbf{n}) are components of the heat flux \mathbf{q} . Moreover, because of objectivities of q and (arbitrary) \mathbf{n} , the heat flux \mathbf{q} is an objective vector (cf. motivation of (3.31) and below (3.72)).²¹ Inserting (3.100) into (3.97) and using (3.68), (3.86) we obtain the balance of the whole energy (internal and kinetic) in the usual form

$$\begin{aligned} \overline{\int_V \rho(u + (1/2)\mathbf{v}^2) dv} &= \overline{\int_V \rho(u + (1/2)\mathbf{v}^2) dv} \\ &= - \int_{\partial V} \mathbf{q} \cdot \mathbf{n} da + \int_V Q dv + \int_{\partial V} \mathbf{v} \cdot \mathbf{T} \mathbf{n} da \\ &\quad + \int_V \rho(\mathbf{b} + \mathbf{i}) \cdot \mathbf{v} dv \end{aligned} \quad (3.102)$$

which is valid in an arbitrary frame (in inertial frame $\mathbf{i} = \mathbf{o}$). Balance (3.102) may be also written for fixed volume V with surface ∂V if we use the Reynolds theorem (3.24)

$$\begin{aligned} \frac{d}{dt} \int_V \rho(u + (1/2)\mathbf{v}^2) dv + \int_{\partial V} \rho(u + (1/2)\mathbf{v}^2) \mathbf{v} \cdot \mathbf{n} da \\ = \int_{\partial V} \mathbf{v} \cdot \mathbf{T} \mathbf{n} da + \int_V \rho(\mathbf{b} + \mathbf{i}) \cdot \mathbf{v} dv - \int_{\partial V} \mathbf{q} \cdot \mathbf{n} da + \int_V Q dv \end{aligned} \quad (3.103)$$

A special case follows when the body force has a potential Φ constant in the time²²

$$\mathbf{b} + \mathbf{i} = -\operatorname{grad}\Phi, \quad \frac{\partial \Phi}{\partial t} = 0 \quad (3.104)$$

Inserting (3.104) into (3.102) and using (3.8), (3.68) we can interpret this special case as the balance of internal, kinetic and potential energy

²⁰ The sign is in accord with convention mentioned in Rem. 7 in Chap. 1: negative heat q is emitted when \mathbf{q} has direction of outer normal \mathbf{n} . Also Fourier law (3.187) directs heat flux \mathbf{q} against temperature gradients, cf. [1, 14, 24, 27, 36, 37].

²¹ Heat is based on molecular motion; therefore the possible nonobjectivity of heat flux has been discussed [24, 38–40]. Because of the molecular chaos this effect is probably negligible with the exception of very rarefied gases. Cf. also Rem. 33 in Chap. 4.

²² Such is, e.g. the potential $\Phi = (1/2)\mathbf{x}^* \cdot \underline{\underline{\Omega}}^2 \mathbf{x}^*$ giving centrifugal force (3.47); $\underline{\underline{\Omega}}^2$ (as a product of the identical skew-symmetrical tensors) is symmetrical.

$$\overline{\int_{\mathcal{V}} \rho(u + (1/2)\mathbf{v}^2 + \Phi) dv} = \int_{\partial\mathcal{V}} \mathbf{v} \cdot \mathbf{Tn} da - \int_{\partial\mathcal{V}} \mathbf{q} \cdot \mathbf{n} da + \int_{\mathcal{V}} Q dv \quad (3.105)$$

Now we can obtain the balance of energy in a local form using (3.68), Gauss' theorem and validity of (3.102) for all \mathcal{V}

$$\overline{\rho(u + (1/2)\mathbf{v}^2)} = -\operatorname{div} \mathbf{q} + Q + \operatorname{div}(\mathbf{vT}) + \rho(\mathbf{b} + \mathbf{i}) \cdot \mathbf{v} \quad (3.106)$$

From this we subtract the balance of “kinetic energy” obtained from (3.78) multiplying it by \mathbf{v} and using (3.14), (3.15), (3.93) to get the *local energy balance*

$$\rho \dot{u} = -\operatorname{div} \mathbf{q} + Q + \operatorname{tr}(\mathbf{TD}) \quad (3.107)$$

(this follows also by localization from (3.97), (3.68), (3.100), (3.98)). This result is valid in any frame because of objectivity of all members here, cf. Sect. 3.2.

We now apply the entropy inequality (1.42) to our continuous body (or arbitrary part of it). Because the integral in (1.42) may be understood (by definition of heat distribution) as time and space integral we can formulate an entropy inequality using the entropy rate, heating and corresponding densities of these quantities (cf. end of Sect. 1.4 and the way we obtained (2.2); again it is possible to proceed more naturally, see Rems. 7, 14 and 18) [11, 18, 35, 41]. Therefore entropy may be expressed if we introduce the *specific entropy* s as a primitive objective scalar. Because the heating now contains surface and volume parts with densities q and Q (cf. (3.97)) and because the absolute temperature is now scalar field $T = T(\mathbf{x}, t)$, assumed to be objective, it follows that the *entropy inequality* may be formulated as (we use (3.100))

$$\overline{\int_{\mathcal{V}} \rho s dv} \geq - \int_{\partial\mathcal{V}} (\mathbf{q}/T) \cdot \mathbf{n} da + \int_{\mathcal{V}} (Q/T) dv \quad (3.108)$$

for the material volume \mathcal{V} with the surface $\partial\mathcal{V}$ of a body or its arbitrary part.²³

By Gauss' theorem and (3.68) we obtain entropy inequality in the local form called the *Clausius-Duhem inequality*

$$\sigma \equiv \rho \dot{s} + \operatorname{div}(\mathbf{q}/T) - Q/T \geq 0 \quad (3.109)$$

valid in any frame. The left-hand side of inequality (3.109) defines the *production of entropy* σ which is therefore never negative and by the objectivity of its defining quantities it is an objective scalar.

Using (3.68), Gauss' theorem (3.23) and definition (3.109) we can write entropy inequality (3.108) as

²³ Using Reynolds theorem (3.24) in (3.108) we obtain quite naturally the entropy inequality for open systems in (single) continua. Cf. Rems. 14 in Chap. 2, 11 in Chap. 4 and the end of Sect. 3.1.

$$\int_{\mathcal{V}} \rho \dot{s} \, dv + \int_{\mathcal{V}} \operatorname{div}(\mathbf{q}/T) \, dv - \int_{\mathcal{V}} (Q/T) \, dv = \int_{\mathcal{V}} \sigma \, dv \geq 0 \quad (3.110)$$

Finally, we can eliminate \mathbf{q} and Q from energy balance (3.107) and Clausius-Duhem inequality (3.109) and use the following definition of the *specific free energy* f and the *temperature gradient* \mathbf{g}

$$f \equiv u - Ts \quad (3.111)$$

$$\mathbf{g} \equiv \operatorname{grad} T \quad (3.112)$$

(it follows that both are objective quantities, cf. Sect. 3.2) to get the *reduced inequality*

$$-T\sigma = \rho \dot{f} + \rho s \dot{T} + T^{-1} \mathbf{q} \cdot \mathbf{g} - \operatorname{tr}(\mathbf{TD}) \leq 0 \quad (3.113)$$

This is again objective and will be useful later in Sect. 3.6.

At the end of these Sects. 3.3 and 3.4 we note that energy balance and entropy inequality motivated by procedures like those in Chap. 1 together with generalization of frame indifference (plausible objectivity is postulated not only for motion (Sect. 3.2) but also, e.g., for power of surface and body forces or heating) permit to deduce balances in Sect. 3.3 (i.e., for mass, linear and angular momentum), internal energy, entropy and their objectivity, etc. For details see, e.g., [1, 22, 42, 43] and other works on modern thermomechanics [7, 8, 18, 20, 41].

Summary. Energy balance containing heat transfer, and entropy inequality are typical thermodynamic conceptions. In fact, they constitute the (general forms of) First and Second Law of thermodynamics, respectively. Perhaps the most important for further development are the local energy balance in the form (3.107) and the Clausius-Duhem formulation of entropy inequality—(3.109). Introducing the (specific) free energy, (3.111), the latter is transformed to the reduced form (3.113).

3.5 Constitutive Principles and Constitutive Equations for the Single Substance

In preceding paragraphs, the balances and the entropy inequality in local form (3.63), (3.76), (3.93), (3.107), (3.109) have been obtained. Because of the general validity of balances (for broad class of nonuniform single continua in a given case; cf. similar situation in Sect. 2.1) these independent relations are not sufficient for determination of all fields (functions of \mathbf{x}, t) occurring there

$$\underline{\chi}, \quad \rho, \quad T \quad (3.114)$$

$$u, \quad s, \quad \mathbf{q}, \quad \mathbf{T} \quad (3.115)$$

$$Q, \quad \mathbf{b}, \quad \mathbf{i} \quad (3.116)$$

We call the fields (3.114)–(3.116) fulfilling the balances of mass (3.63), (3.65), momentum (3.76), moment of momentum (3.93), and energy (3.107) a *thermodynamic process*, because only these are of practical interest. Then we denote the fields (3.114) as the *thermokinetic process* and the fields (3.115) as the *responses* (we limit to the models with symmetric \mathbf{T} (3.93); in more general models we must introduce also the torque \mathbf{M} into responses (3.115), cf. Rems. 17, 32). The fields (3.116) are controlled from the outside²⁴ (at least in principle). Just constitutive equations, which express the difference among materials, represent the missing equations and are relations between (3.114) and (3.115) [6, 7, 9, 10, 23, 34, 38, 40, 41, 44, 45]. Referring to Sect. 2.1 we briefly recall that *constitutive equations* are definitions of ideal materials which approximate real materials in the circumstances studied (i.e., at chosen time and space scales). Constitutive equations may be proposed in rational thermodynamics using the *constitutive principles* of²⁵: *determinism, local action, memory, equipresence, objectivity, symmetry, and admissibility*.

The constitutive principle of *determinism* asserts that responses (3.115) in the present instant and given place are determined by thermokinetic process (3.114) in the past and present in all the body. But in single substances, the field of density is given by the motion through (3.65) (field ρ_0 is assumed to be known) and therefore response (3.115) is given by fields $\underline{\chi}$ and T only (in fact mass balance was used; this will be used also in the following applications of thermokinetic process, cf. Sects. 3.6, 4.5). Thus, the constitutive equations are functionals giving values of (3.115) in given particle \mathbf{X} and present time t , independent variables of which are functions

$$\underline{\chi}(\mathbf{Y}, \tau), \quad T(\mathbf{Y}, \tau) \quad (3.117)$$

in all the particles \mathbf{Y} of the body and all times $\tau \leq t$. This very general material model is significantly reduced by the following two constitutive principles. The principle of *local action* asserts that responses (3.115) are influenced only by values of (3.117) in particles $\mathbf{Y} = \mathbf{X}$ and in immediate neighbourhood of \mathbf{X} (“locality,” cf. Rem. 12 in Chap. 2) and, similarly, the principle of *differential memory* asserts that the response (3.115) is given only by the values (3.117) in the present time t and in the immediate past. Mathematically we can express these principles in the following way (cf. Sect. 2.1 and Rem. 3 in Chap. 2 for memory effect only): we expand (3.117) in the Taylor series around the present time t and given particle \mathbf{X} ; then the response is influenced only by the values and several space and time derivatives taken at these t and \mathbf{X} . This means that the response functionals are reduced to the following functions:

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \check{\mathcal{F}}(\mathbf{x}, \mathbf{v}, \mathbf{F}, \text{Grad}\mathbf{F}, \dot{\mathbf{F}}, T, \text{Grad}T, \mathbf{X}, t) \quad (3.118)$$

²⁴ Such are also boundary values \mathbf{q}, \mathbf{T} on the real surface of the whole body, cf. Rems. 13, 18, see also Rem. 36.

²⁵ Repeating those noted in Sects. 1.1 and 2.1 the name “principles” here is stilted a little: they are rather rules or recommendations which generalize motivation or proposals of such equations in the past [40], cf. exceptions in Rems. 21, 26, and 28.

We believe that the choice of derivatives is representative for the materials intended for study here. Note the elimination of temperature memory; otherwise the “local equilibrium” might be invalid (cf. Sects. 2.2, 4.5).

In (3.118), the concise form of writing of several constitutive equations with the same variables was used, i.e., here $\check{\mathcal{F}}$ stands for constitutive functions \check{s} , \check{u} , $\check{\mathbf{q}}$, $\check{\mathbf{T}}$ respectively (overhead symbol $\check{}$ differs function from its value; rare exclusion, see, e.g., Sect. 3.2). Because the response as well as the independent variables are functions of \mathbf{X} and t , we add in (3.118) also explicit dependence on these quantities.²⁶ In formulation of constitutive equations (3.118) the constitutive principle of *equipresence* was used: in all constitutive equations (3.118) we used the same independent variables. This prevents the unjustified preference of some of such equations; it is a rather plausible rule, cf. Rem. 25, Sect. 2.1, which in special cases, e.g. [28, 60], may be left.

The explicit dependence on \mathbf{X} in (3.118) means that in different particles of our body there may be different material of the same type (i.e., depending on the same variables but in different way). We eliminate for simplicity this dependence, i.e., our body consists of the same material in all particles.²⁷ Then we use (3.14), (3.15), (3.112) to write (3.118) in the form

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \check{\mathcal{F}}(\mathbf{x}, \mathbf{v}, \mathbf{F}, \text{Grad}\mathbf{F}, \mathbf{D}, \mathbf{W}, T, \mathbf{g}, t) \quad (3.119)$$

where $\check{\mathcal{F}}$ means functions \check{s} , \check{u} , $\check{\mathbf{q}}$, $\check{\mathbf{T}}$.

Further reduction of constitutive equations (3.119) may be achieved by the constitutive principle of *frame indifference* or the principle of *objectivity*: the material properties and therefore also constitutive equations must be independent of the choice of frame. This principle is a generalization of common experience with mate-

²⁶ Great numbers of more general models have been studied e.g. with long range memory (as *fading memory* or with *internal variables* mentioned in Sects. 2.1, 2.3), where differential memory is not suitable. Its analog for a space coordinate is the nonlocal material [46–50] where the local action is not sufficient. Another type are materials with a microstructure (*micromorphic* materials) in which the particles have a more complicated structure [11, 45, 48, 51, 52] (cf. Rem. 2). For simplicity we excluded in (3.118) the temperature memory studied in [23, 26, 53] (the influence of which was outlined in Sect. 2.2; cf. Rem. 31 in Chap. 4). The principle of determinism is modified in materials with *internal constraints* [6, 7, 10, 12, 54–58] manifested usually as some a priori limitation on the motion (but there are also nonmechanical constraints such as perfect heat conductivity). Most important are *incompressible* materials where the internal constraint is $J = 1$ (by (3.64) density of particles does not change and therefore only isochoric motions are allowed). The limitation is achieved by forces (pressure in incompressible material) which are not determined by the motion and do not work. The remaining part of the stress is given by the usual principle of determinism. Modification of determinism is also given by using pressure as an independent variable (usual in classical thermodynamics); then incompressibility may be also understood as pressure independence here [24, 59], cf. end of Sect. 3.7.

²⁷ Moreover a unique reference configuration was tacitly assumed in the whole body. But there are (nonfluid, usually solid) materials with *dislocations* which may be just described by nonunique references and dependence on \mathbf{X} remains even if they are from the “same” material, cf. [6, 8, 41], cf. also Rem. 30.

rial properties.²⁸ Mathematically this principle means that the functions in (3.119) (considered in some frame) are the same in the arbitrary other “starred” frame

$$\{s^*, u^*, \mathbf{q}^*, \mathbf{T}^*\} = \check{\mathcal{F}}(\mathbf{x}^*, \mathbf{v}^*, \mathbf{F}^*, (\text{Grad}\mathbf{F})^*, \mathbf{D}^*, \mathbf{W}^*, T^*, \mathbf{g}^*, t^*) \quad (3.120)$$

where starred quantities in the new frame are transformed by (3.25), (3.26), (3.38), (3.49), (3.53), (3.54), (3.51) and (3.30)–(3.32) for objective $s, u, \mathbf{q}, \mathbf{T}, T, \mathbf{g}$.

In a special choice $\mathbf{Q} = \mathbf{1}$ and arbitrary $b, \mathbf{c}, \dot{\mathbf{c}}, \dot{\mathbf{Q}}$, these transformations must give the same values of responses in (3.119) and (3.120) (because $\check{\mathcal{F}}$ is the same in both frames) and this is possible (change from (3.119) to (3.120) is valid for any values of independent variables) only if responses are independent of variables $\mathbf{x}, t, \mathbf{v}$ and \mathbf{W} . This means that two observers with a shift in origins of time and space and with different velocities of translation and rotation must obtain the same responses. Therefore, the constitutive equations (3.119) must be reduced by the principle of frame indifference (or objectivity) to the form

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \bar{\mathcal{F}}(\mathbf{F}, \text{Grad}\mathbf{F}, \mathbf{D}, T, \mathbf{g}) \quad (3.121)$$

where again $\bar{\mathcal{F}}$ means functions $\bar{s}, \bar{u}, \bar{\mathbf{q}}, \bar{\mathbf{T}}$.²⁹ Because responses are given by (3.121) in the actual reference, the $\bar{\mathcal{F}}$ must be such that responses are the same if we only change reference configuration (\mathbf{F} and $\text{Grad}\mathbf{F}$ change correspondingly but describe the same deformation; the other independent variables in (3.121) remain the same [6, 7, 41, 63], cf. Rem. 30 for application).

But this is not all. Using again the change of frame with arbitrary \mathbf{Q} in the constitutive equations (3.121) we have (note that here all dependent and independent variables are objective; we can regard \mathbf{F} and $\text{Grad}\mathbf{F}$ as objective vectors, cf. (3.49), (3.51))

$$\{s, u, \mathbf{Q}\mathbf{q}, \mathbf{Q}\mathbf{T}\mathbf{Q}^T\} = \bar{\mathcal{F}}(\mathbf{Q}\mathbf{F}, \mathbf{Q}\text{Grad}\mathbf{F}, \mathbf{Q}\mathbf{D}\mathbf{Q}^T, T, \mathbf{Q}\mathbf{g}) \quad (3.122)$$

which must be identically valid for any values of independent variables and any orthogonal tensor \mathbf{Q} from the full orthogonal group (see Rem. 8), i.e., at any rota-

²⁸ E.g. we tacitly assume such a principle in the assertion that the same force extends by the same amount the loaded spring when it is suspended in gravitational field or it is attached in the centre of rotated disc. Namely, we assume that the constant of the Hook’s law of the spring (i.e., its constitutive equation) is the same in these both frames [6, 7, 61]. But, cf. Rem. 25, even here they are exceptions [62] (from nonclassical physics).

²⁹ Namely, the substitution described below (3.120) gives

$$\{s, u, \mathbf{Q}\mathbf{q}, \mathbf{Q}\mathbf{T}\mathbf{Q}^T\} = \check{\mathcal{F}}(\mathbf{Q}\mathbf{x} + \mathbf{c}, \mathbf{Q}\mathbf{v} + \dot{\mathbf{c}} + \underline{\Omega}\mathbf{Q}\mathbf{x}, \mathbf{Q}\mathbf{F}, \mathbf{Q}\text{Grad}\mathbf{F}, \mathbf{Q}\mathbf{D}\mathbf{Q}^T, \mathbf{Q}\mathbf{W}\mathbf{Q}^T + \underline{\Omega}, T, \mathbf{Q}\mathbf{g}, t + b)$$

which by choice

$$\mathbf{Q} = \mathbf{1}, \mathbf{c} = -\mathbf{x}, \dot{\mathbf{c}} = -\mathbf{v} + \mathbf{W}\mathbf{x}, \underline{\Omega} = -\mathbf{W}, b = -t$$

gets

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \check{\mathcal{F}}(\mathbf{o}, \mathbf{o}, \mathbf{F}, \text{Grad}\mathbf{F}, \mathbf{D}, \mathbf{0}, T, \mathbf{g}, 0) \equiv \bar{\mathcal{F}}(\mathbf{F}, \text{Grad}\mathbf{F}, \mathbf{D}, T, \mathbf{g})$$

valid for any independent variables, i.e., giving (3.121).

tion and inversion (also restriction on rotation only is used; cf. Rem. 9). This condition (3.122) restricts the form of functions to the so-called *isotropic functions*, the form of which in vector and tensor variables is very limited [6, 9, 64–66] (cf. also Appendix A.2 for linear functions on which we concentrate later, see Sect. 3.7). We name the model with constitutive equations (3.121) the *nonsimple* (or *second grade*) *material with heat conduction and viscosity*.

A special case is a *simple* material which does not depend on $\text{Grad}\mathbf{F}$, cf. [67, 68]

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \bar{\mathcal{F}}(\mathbf{F}, \mathbf{D}, T, \mathbf{g}) \quad (3.123)$$

Such functions $\bar{\mathcal{F}}$ must again be isotropic (for \mathbf{Q} from full orthogonal group)

$$\{s, u, \mathbf{Q}\mathbf{q}, \mathbf{Q}\mathbf{T}\mathbf{Q}^T\} = \bar{\mathcal{F}}(\mathbf{Q}\mathbf{F}, \mathbf{Q}\mathbf{D}\mathbf{Q}^T, T, \mathbf{Q}\mathbf{g}) \quad (3.124)$$

Further simplification of (3.123) is *thermoelastic* material (with heat conductivity, see Sect. 3.6)

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \bar{\mathcal{F}}(\mathbf{F}, T, \mathbf{g}) \quad (3.125)$$

(or *elastic* at T fixed, cf. Rem. 31) again isotropic, i.e., fulfilling analogical conditions (3.124).

The following constitutive principle of *material symmetry* demands that constitutive equations must be in accord with the inherent symmetry of the material studied.

Here we confine mainly to *fluids* (gases or liquids) defined as materials with maximal symmetry. Using this principle we find that dependence on \mathbf{F} and $\text{Grad}\mathbf{F}$ may be in fluids expressed through dependence on density ρ and its gradient \mathbf{h}

$$\mathbf{h} \equiv \text{grad}\rho \quad (3.126)$$

respectively, and constitutive equations are independent of the reference. Other important materials are *solids*, mainly those *isotropic* (not to be confused with the isotropic function!), or crystals of different crystal classes, etc. For the purposes of this book, we plainly define the fluid using ρ instead of \mathbf{F} in (3.125) for a simple fluid, and using ρ, \mathbf{h} instead of $\mathbf{F}, \text{Grad}\mathbf{F}$ in (3.121) for a nonsimple fluid. But such replacement may be deduced.³⁰

³⁰ How the principle of symmetry works we outline on simple material (3.123) (see [6, 7, 10, 14, 41, 63, 69] for details); for nonsimple fluid the similar procedure is more complicated, see [14, 70, 71]. Assume for simplicity a unique reference with reference density ρ_0 in the whole body (everywhere is uniform material without dislocations, see Rem. 27) and all responses behave equally (their symmetries are the same). The material symmetry may be expressed by (referential) tensor \mathbf{H} (in components H^{JK}) which, changing deformation \mathbf{F} to $\mathbf{F}\mathbf{H}$ in constitutive relation (3.123), gives the same response

$$\bar{\mathcal{F}}(\mathbf{F}) = \bar{\mathcal{F}}(\mathbf{F}\mathbf{H}) \quad (a)$$

(nonchanging variables are omitted for brevity) and also the same (actual) density ρ at considered reference density ρ_0 , i.e., by (3.65), (3.12), $\rho_0 = \rho|\det\mathbf{F}| = \rho|\det\mathbf{F}\mathbf{H}|$. This latter condition limits tensors \mathbf{H} to those which are unimodular

Also other criteria for classification of materials may be used.³¹

Therefore constitutive equations of *nonsimple fluid with viscosity and heat conduction* are

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \hat{\mathcal{F}}(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g}) \quad (3.127)$$

where $\hat{\mathcal{F}}$ stands for functions $\hat{s}, \hat{u}, \hat{\mathbf{q}}, \hat{\mathbf{T}}$ (independent variables including ρ and therefore \mathbf{h} are objective, cf. Sect. 3.2). We repeat that response \mathbf{T} here and in all mentioned constitutive functions is a symmetric tensor. Moreover, the principle of objectivity demands that functions $\hat{\mathcal{F}}$ must be isotropic, i.e., for any \mathbf{Q} from full orthogonal group and all values of independent variables the following is valid

(Footnote 30 continued)

$$|\det \mathbf{H}| = 1 \quad (b)$$

E.g. indistinguishable rotation may be described by orthogonal \mathbf{H} ((b) is valid, cf. Rem. 8).

All such \mathbf{H} form the *symmetry group* \mathcal{G} (e.g., two such rotations $\mathbf{H}_1, \mathbf{H}_2$ give indistinguishable rotation $\mathbf{H}_1 \mathbf{H}_2$) which characterize the inherent symmetry of studied material (3.123) in the considered reference configuration. For example, material is isotropic if any rotation (or even inversion) is indistinguishable, i.e., \mathcal{G} contains a proper (or even full) orthogonal group.

Note that a symmetry group depends on a considered reference: its change (which may also alter referential density) generally changes the group. This is described by Noll's rule; for this and other details see, e.g. [10].

A symmetry group of *simple* material divides it in two parts (and each of them in isotropic and anisotropic subparts) [6, 7, 63]:

- simple solids: isotropic or anisotropic (crystal classes like cubic, hexagonal, triclinic etc.)
- simple liquid crystals: isotropic (simple fluids, i.e., gases or liquids) or anisotropic (liquid crystals).

E.g. in *simple solids* there exists a reference the symmetry group of which is contained in (full) orthogonal group; if they are identical then the material is the simple *isotropic* solid.

Simple fluid has a group of symmetry identical to a *unimodular group* (contains all \mathbf{H} with $|\det \mathbf{H}| = 1$); this group is therefore the maximal one and fluids are isotropic (because they contain the orthogonal group, cf. Rem. 8; note that unimodular deformations (indistinguishable in fluids) need not be orthogonal, e.g., isochoric shear). Replacement of \mathbf{F} by ρ follows from (a), (b) by the choice $\mathbf{H} = J^{1/3} \mathbf{F}^{-1}$ (unimodular for given \mathbf{F} : $|\det \mathbf{H}| = |\det(J^{1/3} \mathbf{F}^{-1})| = J |\det \mathbf{F}|^{-1} = 1$). Indeed, by (3.65), the response is

$$\bar{\mathcal{F}}(\mathbf{F}\mathbf{H}) = \bar{\mathcal{F}}((\rho_0/\rho)^{1/3}) \equiv \hat{\mathcal{F}}(\rho) \quad (c)$$

where $\hat{\mathcal{F}}$ is in fact independent of any reference (and its ρ_0) because the response (in actual configuration) must remain the same if the reference (and therefore \mathbf{F}, ρ_0) is changed (cf. remark under (3.121) valid also for (3.123)).

³¹ Besides those based on symmetry in Rem. 30, see e.g., [8], another was used by Haupt [72] according to the size of memory for the stress tensor \mathbf{T} in an isothermal body: materials (mostly solids) are

- (i) elastic: \mathbf{T} is (deformation) rate independent without hysteresis, e.g. (3.125).
- (ii) plastic: \mathbf{T} is rate independent with hysteresis (by appropriate internal variables, cf. Sect. 2.3).
- (iii) viscoelastic: \mathbf{T} is rate dependent without hysteresis, e.g. (3.123).
- (iv) viscoplastic: \mathbf{T} is rate dependent with hysteresis (possible even in equilibrium).

$$\{s, u, \mathbf{Qq}, \mathbf{QTQ}^T\} = \hat{\mathcal{F}}(\rho, \mathbf{Qh}, \mathbf{QDQ}^T, T, \mathbf{Qg}) \quad (3.128)$$

Analogously, starting from (3.123), *simple fluid with viscosity and heat conduction* has the constitutive equations

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \hat{\mathcal{F}}(\rho, \mathbf{D}, T, \mathbf{g}) \quad (3.129)$$

with analogical properties (3.128).

Finally the specialization of (3.125) on fluid leads to

$$\{s, u, \mathbf{q}, \mathbf{T}\} = \hat{\mathcal{F}}(\rho, T, \mathbf{g}) \quad (3.130)$$

with analogical properties (3.128). This is the *thermoelastic fluid* or, in isothermal case, the *elastic fluid* or *ideal (Euler) fluid*.

The final form of constitutive equations for these models (3.125), (3.127), (3.129) will be given in Sect. 3.6 where we use the constitutive principle of admissibility.

Summary. A procedure really specific for the rational thermodynamics is introduced in this section in the form of several principles put forward to derive the thermodynamically consistent constitutive equations. In their most general form, the constitutive equations were proposed as functions (3.118) on the basis of the principles of determinism, local action, differential memory, and equipresence. They were further reduced to the form (3.121) considering the same material throughout the body and applying the principle of objectivity. Because of our interest in fluids only, the constitutive equations were further modified to this material type by means of the principle of material symmetry giving the final form (3.127). Two special types of fluid were defined by (3.129) and (3.130).

3.6 Principle of Admissibility — Constitutive Equations of Single Material. Fluid with Viscosity and Heat Conduction

The last constitutive *principle of admissibility* (or *dissipation* or *entropy principle*) proposed by Coleman and Noll [68] is the most typical for rational thermodynamics [6, 7, 9, 23, 24, 34, 38, 45, 63, 73] (cf. Sects. 2.2, 2.4, 2.5, 3.7, 4.5).

We call a thermodynamic process which is possible in a given material model, i.e., fields (like (3.114)–(3.116)) fulfilling all balances (like (3.65), (3.76), (3.93), (3.107)) combined with proposed constitutive equations an *admissible thermodynamic process*. Now, we want such a process to also fulfil entropy inequality. According to Coleman and Noll [68] (cf. Rem. 5 in Chap. 2) we leave the admissible thermodynamic process arbitrary and restrict the constitutive equations in such a way that the entropy inequality (3.109) is satisfied identically.

Therefore, the constitutive *principle of admissibility* (also called the *principle of dissipation* or *entropy*) may be formulated as follows: entropy inequality must be

satisfied in any admissible thermodynamic process; mathematical justification of this principle was given by Muschik and Ehrentraut [74].

But, because of the validity of balances (3.107) (and remaining balances (3.93), (3.78), (3.63)), the entropy inequality (3.109) may be expressed as reduced inequality (3.113), the constitutive principle of admissibility may be alternatively formulated as follows: reduced inequality (3.113) must be satisfied in any admissible thermodynamic process.

Moreover, as we show in the following examples, an admissible process may be constructed from a thermokinetic process fulfilling the mass balance (using constitutive equations proposed so far and using outside controlled fields like (3.116)). Therefore, the results of the admissibility principle (i.e., simplifications and further properties of constitutive equations) follow from inequality obtained by inserting the constitutive equations into the reduced inequality and by using suitable thermokinetic process (fulfilling the mass balance, cf. above (3.117); there is also alternative method of I-Shih Liu explained in Appendix 5 avoiding the construction of admissible process in complicated cases. As was shown in Appendix 5, this method gives the same results for our fluid models of Sects. 2.2, 3.7, 4.5).

Although fluids are our main interest, first we demonstrate the admissibility principle on thermoelastic material (3.125).

Here the free energy (3.111) used in (3.113) has obviously the following constitutive equation

$$f = \bar{f}(\mathbf{F}, T, \mathbf{g}) \quad (3.131)$$

We calculate \dot{f} using $\overline{\mathbf{F}\mathbf{F}^{-1}} = 0$ and (3.13)–(3.15) and introducing result in (3.113) we obtain (in Cartesian components):

$$\begin{aligned} -T\sigma = & \rho \frac{\partial \bar{f}}{\partial F^{iJ}} F^{jJ} W^{ij} + \left(\rho \frac{\partial \bar{f}}{\partial F^{iJ}} F^{jJ} - T^{ji} \right) D^{ij} + \rho \left(\frac{\partial \bar{f}}{\partial T} + s \right) \dot{T} \\ & + \rho F^{Ji} \frac{\partial \bar{f}}{\partial g^i} \frac{\dot{}}{(\text{Grad}T)^J} - \rho F^{Ki} \frac{\partial \bar{f}}{\partial g^i} (\text{Grad}T)^J F^{Jj} \dot{F}^{jK} + T^{-1} q^i g^i \leq 0 \end{aligned} \quad (3.132)$$

According to the dissipation principle, this inequality must be valid at any admissible thermodynamic process, which in turn, may be obtained from the appropriate thermokinetic process (3.114) fulfilling the mass balance (cf. general procedure sketched above).

Namely, the inequality (3.132) must be valid in an arbitrarily chosen particle \mathbf{X} and (say present) instant t (\mathbf{x} is the place of \mathbf{X} at t according to motion (3.1)) and the following thermokinetic process (cf. (3.114)) may be constructed in any particle \mathbf{Y} and any time τ (with place \mathbf{y}) in the body as follows: for it we use the following expansions about considered \mathbf{X} and present time t

$$\mathbf{y} = \underline{\chi}(\mathbf{Y}, \tau) = \mathbf{x} + \mathbf{F}(\mathbf{Y} - \mathbf{X}) + \dot{\mathbf{F}}(\mathbf{Y} - \mathbf{X})(\tau - t) \quad (3.133)$$

$$T(\mathbf{Y}, \tau) = T + (\text{Grad}T)(\mathbf{Y} - \mathbf{X}) + \overline{(\text{Grad}T)}(\mathbf{Y} - \mathbf{X})(\tau - t) \quad (3.134)$$

where \mathbf{x} , T , \mathbf{F} , $\dot{\mathbf{F}}$, $\text{Grad}T$, $\overline{(\text{Grad}T)}$ are values of these fields and its derivatives taken at \mathbf{X} , t , and the density field follows from mass balance (3.65)

$$\rho(\mathbf{Y}, \tau) = \rho_0(\mathbf{Y}) / |\det \mathbf{F}(\mathbf{Y}, \tau)| \quad (3.135)$$

(cf. above (3.117); it is valid by the field of density in the given reference configuration $\rho_0(\mathbf{Y})$ which is assumed to be known. The fixed mass of the body is then given by (3.58)).

The thermokinetic process (3.133)–(3.135) in thermoelastic material (3.125) fulfilling mass balance generates the admissible thermodynamic process. Indeed, for chosen values of \mathbf{F} , T and $\mathbf{g} = (\text{Grad}T)\mathbf{F}^{-1}$ at \mathbf{X} (or place \mathbf{x}) and t (see (3.13)) the fields of responses (3.115) follow by (3.125); the symmetric response \mathbf{T} fulfils the balance of moment of momentum. Mass balance is satisfied by (3.135) and the balance of momentum (3.78) and energy (3.107) are satisfied by the appropriate choice of external body force $\mathbf{b}(\mathbf{Y}, \tau)$ (or/and inertial force $\mathbf{i}(\mathbf{Y}, \tau)$) and volume heating $Q(\mathbf{Y}, \tau)$ because (3.116) are controlled from the outside.

Therefore, an admissible thermodynamic process exists and is caused by thermokinetic process (3.133)–(3.135); by the admissibility principle the inequality (3.132) must be satisfied. Then this inequality must be satisfied at (arbitrarily chosen) particle \mathbf{X} and instant t by arbitrarily chosen values of mutually independent \mathbf{F} , T , \mathbf{g} (or $\text{Grad}T$) and \mathbf{W} , \mathbf{D} , \dot{T} , $\overline{(\text{Grad}T)}$ (this follows from the independence of derivatives in expansions (3.133), (3.134) and (3.14), (3.15); note that T (and ρ) are positive scalars and \mathbf{D} , \mathbf{W} are symmetric or skew-symmetric tensors, respectively). But the inequality (3.132) depends only linearly on the latter values and therefore members containing them must be zero because of Lemmas A.5.1, A.5.2 from Appendix 5.

Indeed, if we choose \mathbf{F} , T , \mathbf{g} fixed, \mathbf{D} , \mathbf{W} , $\overline{(\text{Grad}T)}$ zero, the following relation follows from Lemma A.5.1

$$\frac{\partial \bar{f}}{\partial T} = -s \quad (3.136)$$

because \dot{T} may be arbitrary scalar (and $\rho > 0$).

Similarly, if we choose $\overline{(\text{Grad}T)}$ arbitrary at \mathbf{F} , T , \mathbf{g} fixed and \mathbf{D} , \mathbf{W} , \dot{T} zero, the following vector must be zero

$$\frac{\partial \bar{f}}{\partial \mathbf{g}} = \mathbf{0} \quad (3.137)$$

by Lemma A.5.1 (applied on components, i.e., we choose the components of vector $\overline{(\text{Grad}T)}^J$ for $J = 1$ arbitrary and for $J = 2, 3$ as zeros; then the first component of vector $\rho F^{-1ji} \frac{\partial \bar{f}}{\partial g^i}$ must be zero. Repeating such application of Lemma A.5.1 for

remaining $J = 2, 3$ we also obtain zeros for the remaining components of this last vector. Because matrix ρF^{Ji} is regular we obtain result (3.137).

Further, we use Lemma A.5.2 (with consequences for symmetric and skew-symmetric tensors). Namely, if we choose \mathbf{D} , $(\overline{\text{Grad}T})$, \dot{T} zero at arbitrary \mathbf{F} , T , \mathbf{g} , the first member in (3.132) must be zero at any skew-symmetric tensor \mathbf{W} , i.e., the following tensor in this member must be symmetric

$$\frac{\partial \bar{f}}{\partial \mathbf{F}} \mathbf{F}^T = \mathbf{F} \left(\frac{\partial \bar{f}}{\partial \mathbf{F}} \right)^T \quad (3.138)$$

By analogical arguments, we obtain from Lemma A.5.2 that the tensor standing at \mathbf{D} in (3.132) must be skew-symmetric. But it is at the same time symmetric (see (3.138), (3.93)) and therefore it is zero.³²

$$\mathbf{T} = \rho \frac{\partial \bar{f}}{\partial \mathbf{F}} \mathbf{F}^T \quad (3.139)$$

Moreover, these results (3.136)–(3.137) are valid identically: at any \mathbf{F} , T , \mathbf{g} and any \mathbf{X} , t . Therefore, (3.131) is reduced to

$$f = \bar{f}(\mathbf{F}, T) \quad (3.140)$$

and (3.136) and (3.139) show that free energy is a potential for entropy and stress, i.e., the corresponding Gibbs equation is valid. Therefore also s (and by (3.111) also u) and \mathbf{T} depend on \mathbf{F} , T only (only heat flux \mathbf{q} depends on temperature gradient \mathbf{g}).

Production of entropy is caused only by heat conduction

$$\sigma = -T^{-2} \mathbf{q} \cdot \mathbf{g} \geq 0 \quad (3.141)$$

and it is zero in the *equilibrium process* defined here by

$$\mathbf{g} = \mathbf{0} \quad (3.142)$$

(cf. the end of Sect. 2.1 and Rem. 11 in Chap. 1). But in equilibrium (3.142) the production of entropy $\sigma = \bar{\sigma}(\mathbf{F}, T, \mathbf{g})$ (cf. (3.125)) has a minimum and therefore

$$\frac{d}{d\lambda} \bar{\sigma}(\mathbf{F}, T, \lambda \mathbf{g}) |_{\lambda=0} = 0 \quad (3.143)$$

where λ is a real parameter. Inserting (3.141) into (3.143) gives

³² Note that by analogical calculation for (mechanically) polar materials Rem. 17, the result (3.139) is valid but its skew-symmetric part gives torque \mathbf{M} .

$$\mathbf{q}^o \equiv \bar{\mathbf{q}}(\mathbf{F}, T, \mathbf{o}) = \mathbf{o} \quad (3.144)$$

and therefore equilibrium value \mathbf{q}^o of the heat flux is zero.

Without going into details we note also that sufficient conditions of minima of $\bar{\sigma}$ may be discussed and further simplifications of these results using objectivity (3.124) and material symmetry may be obtained: using Cauchy-Green tensors, Piola-Kirchhoff stress tensors, the known linearized constitutive equations of solids follow, e.g. Hook and Fourier laws with tensor (transport) coefficients which are reduced to scalars in isotropic solids (e.g. Cauchy law of deformation with Lamé coefficients) [6, 7, 9, 13, 14].

Results for thermoelastic fluid might be also obtained by the constitutive principle of symmetry but we get them directly from the following fluid model, cf. (3.182) and the end of this section.

Our main goal is to apply the admissibility principle to fluids [39, 53, 75–78], namely to nonsimple fluid (3.127) (the special cases of simple (3.129) and thermoelastic (3.130) fluids will be discussed at the end of this section but the most important are fluids with linear transport properties contained in Sects. 3.7 and 3.8). In nonsimple fluid (3.127) it is sufficient to use the field of velocity (instead of motion), cf. (3.14), (3.15). Therefore we define the *thermokinetic* process in fluids as the fields of (instead of (3.114))

$$\mathbf{v}, \rho, T \quad (3.145)$$

An admissible thermodynamic process in fluids is defined as fields of thermokinetic process (3.145), responses (3.115) (given by constitutive equations (3.127)), and outside fields (3.116) which fulfil balances (3.63), (3.78), (3.93), (3.107).

Although the spatial (Euler) description \mathbf{x}, t is simpler in fluids, the material (time) derivative, expressed by (3.8), is preferred below because it gives more concise results.

The principle of admissibility demands to fulfil entropy inequality (3.109) and therefore also the reduced inequality (3.113) by any admissible thermodynamic process. Here the free energy (3.111) is used for which, as follows from (3.127), we have the following constitutive equation

$$f = \hat{f}(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g}) \quad (3.146)$$

in our nonsimple fluid. Hence we can write

$$\dot{f} = \frac{\partial \hat{f}}{\partial \rho} \dot{\rho} + \frac{\partial \hat{f}}{\partial \mathbf{h}} \cdot \dot{\mathbf{h}} + \text{tr} \frac{\partial \hat{f}}{\partial \mathbf{D}} \dot{\mathbf{D}} + \frac{\partial \hat{f}}{\partial T} \dot{T} + \frac{\partial \hat{f}}{\partial \mathbf{g}} \cdot \dot{\mathbf{g}} \quad (3.147)$$

Here $\text{tr} \frac{\partial \hat{f}}{\partial \mathbf{D}} \dot{\mathbf{D}} = \frac{\partial \hat{f}}{\partial D^{ij}} \dot{D}^{ij}$ where both tensors are symmetric. This is clear for $\dot{\mathbf{D}}$ but the symmetry of $\frac{\partial \hat{f}}{\partial \mathbf{D}}$ follows from the rule that the derivative of a scalar function with respect to a symmetric tensor is symmetric.³³

Now we express $\dot{\rho}$ from (3.63) using (3.16) and $\dot{\mathbf{h}}$ from

$$\dot{\mathbf{h}} = -\mathbf{h}(\mathbf{D} + \mathbf{W}) - \mathbf{h} \text{tr} \mathbf{D} - \rho \text{grad}(\text{tr} \mathbf{D}) \quad (3.148)$$

which may be obtained if we take the gradient from balance of mass (3.62) and use (3.126), (3.9), (3.14), (3.15). Both $\dot{\rho}$ and $\dot{\mathbf{h}}$ we use in (3.147) and then we insert \hat{f} into reduced inequality (3.113). After rearrangement we obtain (in component form)

$$\begin{aligned} -T\sigma = & -\rho \frac{\partial \hat{f}}{\partial h^i} \left(h^j (D^{ji} + W^{ji}) + h^i D^{kk} \right) - \rho^2 \frac{\partial \hat{f}}{\partial h^i} \frac{\partial D^{kk}}{\partial x^i} + \rho \frac{\partial \hat{f}}{\partial D^{ij}} \dot{D}^{ji} \\ & + \rho \frac{\partial \hat{f}}{\partial g^i} \dot{g}^i + \rho \left(\frac{\partial \hat{f}}{\partial T} + s \right) \dot{T} - \left(T^{ij} + \rho^2 \frac{\partial \hat{f}}{\partial \rho} \delta^{ij} \right) D^{ji} + T^{-1} q^i g^i \leq 0 \end{aligned} \quad (3.149)$$

³³ Let f be a scalar function \tilde{f} of symmetric tensor D , i.e., a function of 6 independent variables:

$$\begin{aligned} f = \tilde{f}(\mathbf{D}) = \tilde{f}(D^{11}, D^{12}, D^{13}, D^{22}, D^{23}, D^{33}) &= \tilde{f}(D^{11}, \frac{1}{2}(D^{12} + D^{21}), \\ &\frac{1}{2}(D^{13} + D^{31}), D^{22}, \frac{1}{2}(D^{23} + D^{32}), D^{33}) \\ &\equiv \hat{f}(D^{11}, D^{12}, D^{13}, D^{21}, D^{22}, D^{23}, D^{31}, D^{32}, D^{33}) = \hat{f}(\mathbf{D}) \end{aligned}$$

The last definition of function \hat{f} of 9 variables (allowed by symmetry of \mathbf{D}) permits to employ the customary tensor (or matrix) descriptions, e.g. the summation convention in component form. This is the reason for using this definition of \hat{f} in (3.146), (3.147) and other formulae in this book (similar definitions may be used for skew-symmetric tensor and vector and tensor functions [7, 14, 79]). As may be seen from the definition above, the main property of \hat{f} is (when \mathbf{D} is symmetrical and this is just such a case) that $\frac{\partial \hat{f}}{\partial \mathbf{D}}$ is indeed symmetrical, e.g.

$$\frac{\partial \hat{f}}{\partial D^{12}} = \frac{1}{2} \frac{\partial \tilde{f}}{\partial D^{12}} = \frac{\partial \tilde{f}}{\partial D^{21}}$$

If \mathbf{B} is a symmetric tensor then, as may be expected,

$$\begin{aligned} \text{tr} \frac{\partial \hat{f}}{\partial \mathbf{D}} \mathbf{B} &= \frac{\partial \hat{f}}{\partial D^{ij}} B^{ji} = \frac{\partial \tilde{f}}{\partial D^{11}} B^{11} + \frac{\partial \tilde{f}}{\partial D^{12}} B^{12} + \frac{\partial \tilde{f}}{\partial D^{13}} B^{13} \\ &+ \frac{\partial \tilde{f}}{\partial D^{22}} B^{22} + \frac{\partial \tilde{f}}{\partial D^{23}} B^{23} + \frac{\partial \tilde{f}}{\partial D^{33}} B^{33} = \frac{\partial \tilde{f}}{\partial \mathbf{D}} \cdot \mathbf{B} \end{aligned}$$

and therefore this expression may be also written as an inner product in the space of symmetric tensors, i.e., as a scalar product (denoted by dot) of 6-dimensional vectors. This way is also often used; then, of course, we understand (in (3.146) etc.) f as a function in the space of symmetric tensor \mathbf{D} , i.e., as \tilde{f} . Similarly it may be proved that the derivative of a scalar function with respect to a skew-symmetric tensor is again skew-symmetric.

This inequality depends through constitutive equations (3.127), (3.146) on

$$\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g} \quad (3.150)$$

and linearly on

$$\mathbf{W}, \text{grad tr} \mathbf{D}, \dot{\mathbf{D}}, \dot{T}, \dot{\mathbf{g}} \quad (3.151)$$

In accord with our general procedure sketched in the beginning of this section we now construct the following thermokinetic process (assumed to fulfil mass balance) which generates an admissible thermodynamic process which in turn, by the admissibility principle, must fulfil the inequality (3.149). From this then further properties of constitutive equations (3.127), (3.146) will be obtained.

Namely, we construct the thermokinetic process (3.145) in arbitrary point \mathbf{y} of the actual configuration of the body and arbitrary instant τ as bounded expansions of fields $\mathbf{v}(\mathbf{y}, \tau)$, $T(\mathbf{y}, \tau)$ around the arbitrarily selected place \mathbf{x} in the body and (present) instant t

$$\begin{aligned} v^i(\mathbf{y}, \tau) = & v^i(\mathbf{x}, t) + (L^{ij}(\mathbf{x}, t))(y^j - x^j) + \left(\frac{\partial L^{ij}}{\partial t}(\mathbf{x}, t) \right) (y^j - x^j)(\tau - t) \\ & + \frac{1}{2} \left(\frac{\partial L^{ij}}{\partial x^k}(\mathbf{x}, t) \right) (y^j - x^j)(y^k - x^k) \end{aligned} \quad (3.152)$$

$$\begin{aligned} T(\mathbf{y}, \tau) = & T(\mathbf{x}, t) + (\mathbf{g}(\mathbf{x}, t)) \cdot (\mathbf{y} - \mathbf{x}) + \left(\frac{\partial T}{\partial t}(\mathbf{x}, t) \right) (\tau - t) \\ & + \left(\frac{\partial \mathbf{g}}{\partial t}(\mathbf{x}, t) \right) \cdot (\mathbf{y} - \mathbf{x})(\tau - t) \end{aligned} \quad (3.153)$$

Density field $\rho(\mathbf{y}, \tau)$ need not be formulated explicitly because mass balance is assumed to be valid (in fact it has been assumed at deduction of (3.149) in eliminations of $\dot{\rho}$, $\dot{\mathbf{h}}$ by (3.63), (3.148); note that $\dot{\rho}$, $\dot{\mathbf{h}}$ are not present in (3.150), (3.151)). It is satisfied, e.g. as (3.63) by choice $\overline{\ln \rho} = \dot{\rho}/\rho = -\text{div} \mathbf{v}$ for appropriate velocity (3.152) at any \mathbf{y} , τ .³⁴

This thermokinetic process (with validity of mass balance) generates an admissible thermodynamic process: we can obtain the values of independent variables of constitutive equations (3.127), (3.146) in the whole body at any time (see (3.126), (3.112), (3.15)) and therefore also fields of responses (3.115) (with f). Further the balance of moment of momentum (3.93) is satisfied because of symmetric tensor \mathbf{T}

³⁴ Construction of $\rho(\mathbf{y}, \tau)$ in Euler description is more complicated: in principle we can use current deformation of the body in present time t (assumed to be known as well as density fields $\rho(\mathbf{y}, t)$ in it) as the reference, calculate relative deformation function $\mathbf{y} = \underline{\chi}_t(\mathbf{x}, \tau)$ (cf. (3.1)) by integration of velocity field (3.152) and in turn the relative deformation gradient $\mathbf{F}_t = \text{grad} \underline{\chi}_t$ (see [8] p. 9 for details or [7, 10]). Then $\rho(\mathbf{y}, \tau) = \rho(\mathbf{y}, t) / |\det \mathbf{F}_t(\mathbf{y}, \tau)|$ following analogy with (3.65).

in (3.127) and ultimately balances of momentum (3.78) and energy (3.107) may be fulfilled if we use appropriate fields of body force \mathbf{b} (or/and inertial force \mathbf{i}) and body heating Q respectively.

Thus for each choice of obviously mutually independent values of \mathbf{v} and T and its derivatives in (3.152), (3.153) taken in some \mathbf{x} and t the admissible thermodynamic process exists and, according to the constitutive principle of admissibility, the reduced inequality (3.113) and therefore inequality (3.149) must be valid in this \mathbf{x}, t .

We choose these quantities in \mathbf{x}, t as follow: density and its gradient have the values ρ, \mathbf{h} , fields (3.152), (3.153) and its derivatives have values T, \mathbf{g} and

$$\mathbf{v}(\mathbf{x}, t) = \mathbf{0}, \quad \mathbf{L}(\mathbf{x}, t) = \mathbf{D} + \mathbf{W}, \quad \frac{\partial \mathbf{L}}{\partial t}(\mathbf{x}, t) = \dot{\mathbf{D}}$$

$$\frac{\partial L^{ij}}{\partial x^k} = \frac{1}{3} \frac{\partial D^{ll}}{\partial x^k} \delta^{ij}$$

(δ^{ij} is Kronecker delta),

$$\frac{\partial T}{\partial t} = \dot{T}, \quad \frac{\partial \mathbf{g}}{\partial t} = \dot{\mathbf{g}}, \quad \frac{\partial \rho}{\partial t} = -\rho \operatorname{tr} \mathbf{D} - \mathbf{v} \cdot \mathbf{h} = -\rho \operatorname{tr} \mathbf{D}$$

This choice of (3.150), (3.151) may be arbitrary and independent (ρ, T are positive scalars, $\mathbf{D}, \dot{\mathbf{D}}$ are symmetric tensors, \mathbf{W} skew-symmetric tensor and $\dot{T}, \mathbf{h}, \mathbf{g}$, $\operatorname{grad} \operatorname{tr} \mathbf{D}, \dot{\mathbf{g}}$ are arbitrary scalar or vectors); here the zero velocity in \mathbf{x}, t was used (see (3.8), (3.9)) and the choice of value $\frac{\partial \rho}{\partial t}$ (not needed in (3.149)) simply expresses the mass balance (3.62) at \mathbf{x}, t .

But because (3.149) depends on values (3.151) linearly, we can use Lemma A.5.1 from Appendix A.5, and the following restrictions on the constitutive equations follow

$$\frac{\partial \hat{f}}{\partial \mathbf{h}} = \mathbf{0}, \quad \frac{\partial \hat{f}}{\partial \mathbf{D}} = \mathbf{0}, \quad \frac{\partial \hat{f}}{\partial \mathbf{g}} = \mathbf{0} \quad (3.154)$$

$$\frac{\partial \hat{f}}{\partial T} = -s \quad (3.155)$$

$$-T\sigma = T^{-1} \mathbf{q} \cdot \mathbf{g} - \operatorname{tr} \left(\left(\mathbf{T} + \rho^2 \frac{\partial \hat{f}}{\partial \rho} \mathbf{1} \right) \mathbf{D} \right) \leq 0 \quad (3.156)$$

E.g. to prove (3.154)₁ we choose (3.150) and $\mathbf{W}, \dot{\mathbf{D}}, \dot{T}, \dot{\mathbf{g}}$ as some constants in Lemma A.5.1 applied on components (similarly as in proof of (3.137)): we choose the 1st component of $\operatorname{grad} \operatorname{tr} \mathbf{D}$ as arbitrary reals, while its 2nd and 3rd component are selected equal to zero. Then the result $\frac{\partial \hat{f}}{\partial h^1} = 0$ follows from Lemma A.5.1 (ρ are always positive). By repetition of this procedure for remaining components 2,3 analogously we obtain the results (3.154)₁.

By a similar procedure we obtain (3.154)₂: we choose (3.150) and fixed \mathbf{W} , \dot{T} , $\dot{\mathbf{g}}$ (and $\text{grad tr} \mathbf{D}$ or we use the previous result) and because $\text{tr} \frac{\partial \hat{f}}{\partial \mathbf{D}} \mathbf{D}$ may be considered as a 6-dimensional scalar product, cf. Rem. 33, we obtain by Lemma A.5.1 the result (3.154)₂ analogously as in the previous case. But we can use equivalently Lemma A.5.2 understanding \mathbf{D} as 3×3 symmetric tensor: because \mathbf{D} is symmetric, the tensor $\frac{\partial \hat{f}}{\partial \mathbf{D}}$ is skew-symmetric but at the same time it is symmetric (cf. Rem. 33) and therefore zero (3.154)₂.

Quite similarly we obtain the remaining results (3.154)₃, (3.155). Thus the original entropy production (3.149) is simplified to inequality (3.156).

Note that the same results follow using the I-Shih Liu method of Lagrange multipliers (see Appendix A.5) and the discussion of mass balance in the construction of an admissible process is not needed. This method is described in Appendix A.5 in the example of thermoelastic simple fluid, cf. (3.11).

Relations (3.154), (3.155) are valid identically because values (3.150) and \mathbf{x} , t are chosen arbitrarily. Therefore the free energy f and also the entropy s (and by (3.111) also u) depend on ρ and T only in the nonsimple fluid

$$f = \hat{f}(\rho, T) \quad (3.157)$$

$$s = \hat{s}(\rho, T) \quad (3.158)$$

We say that in a given place and instant there is an *equilibrium process* when

$$\mathbf{D} = \mathbf{0}, \quad \mathbf{g} = \mathbf{0} \quad (3.159)$$

The motivation for such definition is that the entropy production (3.156) is zero (cf. end of Sect. 2.1 and Rem. 12 in Chap. 1); we omit for simplicity more detailed discussion of equilibrium, reversibility, regularity (cf. Sect. 2.2), because this may be done analogously as in the special case of the linear fluid in Sect. 3.8.

We denote the equilibrium values of stress tensor and heat flux by \mathbf{T}^o and \mathbf{q}^o respectively

$$\mathbf{T}^o = \hat{\mathbf{T}}^o(\rho, \mathbf{h}, T) \equiv \hat{\mathbf{T}}(\rho, \mathbf{h}, \mathbf{0}, T, \mathbf{o}) \quad (3.160)$$

$$\mathbf{q}^o = \hat{\mathbf{q}}^o(\rho, \mathbf{h}, T) \equiv \hat{\mathbf{q}}(\rho, \mathbf{h}, \mathbf{0}, T, \mathbf{o}) \quad (3.161)$$

and we define the nonequilibrium stress tensor \mathbf{T}_N by

$$\mathbf{T}_N = \hat{\mathbf{T}}_N(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g}) \equiv \mathbf{T} - \mathbf{T}^o \quad (3.162)$$

We note that both stresses \mathbf{T}^o and \mathbf{T}_N are symmetrical and equilibrium value of \mathbf{T}_N is zero

$$\mathbf{T}_N^o \equiv \hat{\mathbf{T}}_N(\rho, \mathbf{h}, \mathbf{0}, T, \mathbf{o}) = \mathbf{0} \quad (3.163)$$

Inserting (3.162) into (3.156) we have

$$\sigma = T^{-1} \text{tr} \left(\left(\mathbf{T}^o + \rho^2 \frac{\partial \hat{f}}{\partial \rho} \mathbf{1} \right) \mathbf{D} \right) + T^{-1} \text{tr}(\mathbf{T}_N \mathbf{D}) - T^{-2} \mathbf{q} \cdot \mathbf{g} \geq 0 \quad (3.164)$$

Production of entropy $\sigma = \hat{\sigma}(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g})$ is not only zero but also minimal at equilibrium (3.159). Therefore the following conditions must be fulfilled

$$\frac{d}{d\lambda} \hat{\sigma}(\rho, \mathbf{h}, \lambda \mathbf{D}, T, \lambda \mathbf{g}) \big|_{\lambda=0} = 0 \quad (3.165)$$

$$\frac{d^2}{d\lambda^2} \hat{\sigma}(\rho, \mathbf{h}, \lambda \mathbf{D}, T, \lambda \mathbf{g}) \big|_{\lambda=0} \geq 0 \quad (3.166)$$

where λ is a real parameter (values of $\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g}$ may be fixed arbitrarily).

Inserting (3.164) into (3.165) and using (3.163) we get

$$T^{-1} \text{tr} \left(\left(\mathbf{T}^o + \rho^2 \frac{\partial \hat{f}}{\partial \rho} \mathbf{1} \right) \mathbf{D} \right) - T^{-2} \mathbf{q}^o \cdot \mathbf{g} = 0 \quad (3.167)$$

This equality is linear in arbitrary independent values of \mathbf{D} and \mathbf{g} and therefore we obtain, by Lemmas A.5.1, A.5.2, identities ((3.167) is valid for any ρ, \mathbf{h}, T)

$$\mathbf{T}^o = -P \mathbf{1} \quad (3.168)$$

$$P = \hat{P}(\rho, T) \equiv \rho^2 \frac{\partial \hat{f}}{\partial \rho} \quad (3.169)$$

where P is called the (equilibrium) *pressure* which, as well as \mathbf{T}^o , is function of only ρ and T as follows from (3.157). Further it follows from (3.167) that the equilibrium value of the heat flux is zero

$$\mathbf{q}^o = \hat{\mathbf{q}}(\rho, \mathbf{h}, \mathbf{0}, T, \mathbf{o}) = \mathbf{o} \quad (3.170)$$

The condition (3.166) gives some restrictions on the sign of derivatives of \mathbf{T}_N and \mathbf{q} but we omit them here (we elaborate on them only in the linearized model in Sect. 3.7).

As a result of all constitutive principles the constitutive equations of *nonsimple fluid* with (nonlinear) viscosity and heat conduction are (see (3.111), (3.127), (3.157), (3.158), (3.162), (3.168), (3.169))

$$f = \hat{f}(\rho, T), \quad s = \hat{s}(\rho, T), \quad u = \hat{u}(\rho, T) \quad (3.171)$$

$$\mathbf{q} = \hat{\mathbf{q}}(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g}) \quad (3.172)$$

$$\mathbf{T} = -\hat{P}(\rho, T)\mathbf{1} + \hat{\mathbf{T}}_N(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g}) \quad (3.173)$$

with the properties (3.155), (3.169):

$$\frac{\partial \hat{f}}{\partial T} = -s \quad (3.174)$$

$$\rho^2 \frac{\partial \hat{f}}{\partial \rho} = P \quad (3.175)$$

Functions $\hat{\mathbf{q}}$ and $\hat{\mathbf{T}}_N$ are isotropic (see (3.128), (3.173), Rem. 8), i.e., for every orthogonal tensor \mathbf{Q} we have

$$\mathbf{Q}\hat{\mathbf{q}}(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g}) = \hat{\mathbf{q}}(\rho, \mathbf{Q}\mathbf{h}, \mathbf{Q}\mathbf{D}\mathbf{Q}^T, T, \mathbf{Q}\mathbf{g}) \quad (3.176)$$

$$\mathbf{Q}\hat{\mathbf{T}}_N(\rho, \mathbf{h}, \mathbf{D}, T, \mathbf{g})\mathbf{Q}^T = \hat{\mathbf{T}}_N(\rho, \mathbf{Q}\mathbf{h}, \mathbf{Q}\mathbf{D}\mathbf{Q}^T, T, \mathbf{Q}\mathbf{g}) \quad (3.177)$$

Entropy production is caused by nonequilibrium stress (viscosity) and heat flux (conduction of heat) (see (3.164), (3.168), (3.169))

$$T\sigma = \text{tr}(\mathbf{T}_N\mathbf{D}) - T^{-1}\mathbf{q}\cdot\mathbf{g} \geq 0 \quad (3.178)$$

In the equilibrium process defined by $\mathbf{D} = \mathbf{0}$, $\mathbf{g} = \mathbf{o}$ (3.159), entropy production is zero $\sigma = 0$, stress is reduced on pressure P and heat flux is zero

$$\mathbf{T}^o = -P\mathbf{1} \quad \text{or} \quad \mathbf{T}_N^o = \mathbf{0} \quad (3.179)$$

$$\mathbf{q}^o = \mathbf{o} \quad (3.180)$$

Isotropic functions (cf. (3.176), (3.177)) permit only a certain combination of vectors and tensors on which \mathbf{q} and \mathbf{T} , may depend. This is described by the so called *representation theorems* [6, 9, 23, 64]; for general dependence see [65] (for full and proper orthogonal group from Rem. 8). An example for a simple fluid is given in Rem. 35 below, more details (as well as discussion of other results, e.g. (3.166)) we leave to the special model of linear fluid in Sect. 3.7.

The assertion that the results (3.171) with properties (3.174), (3.175) (in fact the same as in classical thermodynamics and proved in this model of nonsimple fluid) are valid even at nonequilibrium process (at nonzero σ in (3.178)) is known as *local equilibrium*. This was taken as a starting principle in the classical theories of nonequilibrium processes [36, 80]. But in more complicated models local equilibrium need not be valid, cf. Sect. 2.2.

Now we turn to the less complicated case of constitutive equations (3.129)—*simple fluid* with (nonlinear) viscosity and heat conduction in which an independence of the density gradient \mathbf{h} was assumed from the start. By inspection of the results of

the preceding more complicated model we obtain the same results (3.171)–(3.180) with the exceptions that the heat flux \mathbf{q} and nonequilibrium stress \mathbf{T}_N (Eqs. (3.172), (3.173)) are independent of density gradient \mathbf{h} . Flows of such simple fluids are often studied in *rheology*.³⁵

The last specialization is the *thermoelastic simple fluid* excluding also a dependence on \mathbf{D} in constitutive equations of simple fluid (3.129) (independent of \mathbf{h}). Then the results (3.171) are valid, heat flux in (3.172) is independent of \mathbf{h} and \mathbf{D} and nonequilibrium stress \mathbf{T}_N are identically zero, i.e., instead of (3.173) we have

$$\mathbf{T} = -\hat{P}(\rho, T) \mathbf{1} \quad (3.181)$$

with (3.174) and (3.175). Production of entropy (3.178) is reduced to $T\sigma = -T^{-1}\mathbf{q}\cdot\mathbf{g} \geq 0$. This model was used in Appendix A.5 to demonstrate I-Shih Liu method with more constraints giving the same results, cf. (A.158).

All the results for the thermoelastic fluid follow also from (3.136)–(3.144) for thermoelastic materials if we use the constitutive principle of symmetry (cf. Sect. 3.5 and Rem. 30). In this case the constitutive equations (3.125), (3.131) are realized through (3.65), (3.12), e.g.

$$\bar{f}(\mathbf{F}, T, \mathbf{g}) \equiv \hat{f}(\rho_0 | \det \mathbf{F} |^{-1}, T, \mathbf{g}) \quad (3.182)$$

Using (3.182) in (3.139) with the use of (e) from Rem. 4, we deduce (3.181), and (3.175) as well as the other results for thermoelastic fluid.

All these models may be specialized also to *incompressible* fluids, which practically model liquids (at nonextreme, say atmospheric, pressures). Such fluids may be defined mechanically by $J = 1$ [10, 83], cf. Rems. 26, 35 or thermodynamically [24, 43] and this will be discussed at the end of Sect. 3.7.

Further simplification of these fluid models (3.172)–(3.180) we obtain by linearization presented in Sect. 3.7. We note that the formulae (3.198)–(3.207) are valid also in the nonlinear model of this section.

³⁵ Consider an example of the *non-Newtonian liquid* (e.g., solutions and melts of polymers, suspensions, etc.), isothermal and without heat conduction for simplicity. Isotropic nonequilibrium stress fulfils (cf. (3.177))

$$\mathbf{Q}\hat{\mathbf{T}}_N(\rho, \mathbf{D})\mathbf{Q}^T = \hat{\mathbf{T}}_N(\rho, \mathbf{Q}\mathbf{D}\mathbf{Q}^T)$$

for any $\mathbf{Q} \in \mathcal{O}$. Representation theorem of this symmetric isotropic nonlinear function of symmetric tensor is (see [9, 12, 64])

$$\mathbf{T}_N = \gamma_0 \mathbf{1} + \gamma_1 \mathbf{D} + \gamma_2 \mathbf{D}^2$$

where coefficients $\gamma_0, \gamma_1, \gamma_2$ are (nonlinear) functions of ρ (T is constant) and $\text{tr}\mathbf{D}, \text{tr}\mathbf{D}^2, \text{tr}\mathbf{D}^3$. Such non-Newtonian liquid is practically incompressible ($\text{tr}\mathbf{D} = 0$, see Rem. 26, (3.17), (3.16), below and end of Sect. 3.7), γ_0 may be included in the undetermined pressure and for small velocity gradients the last member may be neglected. Constitutive equation for nonequilibrium stress is reduced to [81]

$$\mathbf{T}_N = \gamma_1 \mathbf{D}$$

where γ_1 depends nonlinearly on $\text{tr}\mathbf{D}^2$ (and ρ, T). For more complicated models see [8, 10, 82].

Ultimately these fluid models may still be reduced to the uniform models discussed in Chap. 2 mainly as the model A or B in Sects. 2.1 and 2.2. Due to the uniformity, the dependence on the gradient \mathbf{g} must be eliminated and the dependence on \mathbf{D} should be expressed through $\text{tr}\mathbf{D}$, i.e., through $\dot{\rho}$ or equivalently \dot{V} (see (3.63), (3.16)).

Because of neglecting the motion in the uniform models, the pressure (stress) on the boundary of the body (usually defined from the outside as a boundary condition, cf. Rem. 13) is given by the constitutive equation of material inside the body,³⁶ cf. Rems. 9 in Chap. 1, 1 in Chap. 2 and 37 in this chapter.

Generally, the results for simpler models may be obtained from a more general model by specialization of constitutive equations, but sometimes to get all the results, we must again use the admissibility principle on the remaining inequality (entropy production) of the more complicated model (cf. deduction of (3.181) and also Sect. 3.7).

Summary. This section finalizes the exemplification of rational thermodynamics methodology applying its most typical principle—the principle of admissibility. In fact, this principle represents the requirement of consistency of a material model (constitutive equations) with the Second Law or the entropy inequality. It was applied to finish the derivation of constitutive equations for a single fluid initiated in preceding sections of this chapter. Starting with the form (3.146) for the free energy we arrived at its final simplification in the form (3.157) which indicates also the final constitutive equations for the (specific) entropy and internal energy, see (3.171). In contrast the constitutive equation for the heat flux was not simplified and remained in the form (3.172). The same conclusion was found for the stress tensor but this could be decomposed to equilibrium and nonequilibrium parts, cf. (3.173), the former leading to the (equilibrium) pressure known from classical thermodynamics. Both, pressure and specific entropy are related to (specific) free energy in the form of its derivatives, see (3.174), (3.175). The final form of entropy inequality in this material model is (3.178); the definition of equilibrium, (3.159), is motivated by zero entropy production. Note that during the derivation of constitutive equations not only the entropy inequality as such was applied but also the fact of zero and minimum entropy in equilibrium was used, cf. (3.165) and (3.166). Several simplified fluid models were mentioned at the end of this section. The exposition is thus prepared to derive the key fluid model of our book in the subsequent section.

³⁶ Namely, neglecting the motion and external fields (\mathbf{v} , $\dot{\mathbf{v}}$, \mathbf{b} , \mathbf{i} are practically zeros) the momentum balance (3.81) of the thin layer along the real boundary reduces to $\int_V \mathbf{Tn} \, dv = \mathbf{o}$ with (mostly) pressure P , $\mathbf{T} = -P\mathbf{1}$ (cf. [84], figure on p. 108). In the limit of this narrow sub body this balance expresses the action-reaction law; therefore the pressure from the outside is given by the constitutive equation of the fluid inside (under the boundary). Pressure P in the model B is given by (2.7)₃ (the pressure may contain here a nonequilibrium part (2.34) given (in linear approximation) by the volume viscosity, cf. Rems. 9 in Chap. 1, 1 and 8 in Chap. 2, 37 in this chapter).

The equilibrium pressure part is given by the state equation, see (2.33), (2.32). This, in fact “equilibrium” pressure in “reversible” processes, forms the whole pressure (2.6)₃ of the “classical” thermodynamic model A (density of uniform body with constant mass is given by its volume V).

3.7 Fluid with Linear Transport Properties

In this paragraph we specialize the results for the nonsimple fluid (3.171)–(3.180) on the linear dependence in vectors and tensors i.e., in \mathbf{D} , \mathbf{g} and \mathbf{h} (while the dependence on scalars ρ , T may be nonlinear) [9, 14, 23, 24, 27, 45]. We denote this model as a *linear fluid* or *fluid with linear transport properties* because the results describe the classical Navier-Stokes (Newtonian) and Fourier fluid with linear viscosity and heat conduction; at the same time the classical thermodynamic relations (local equilibrium) are valid.

From the principle of objectivity it follows that functions $\hat{\mathbf{q}}$ and $\hat{\mathbf{T}}_N$ must be isotropic (3.176), (3.177). In the linear case the most general form of such isotropic functions is given by the representation theorem (see Appendix A.2) of vector and tensor functions (3.172), (3.162) which are linear in vectors and tensors (cf. (A.58), (A.68)):

$$\mathbf{q} = -k\mathbf{g} + \chi\mathbf{h} \quad (3.183)$$

$$\mathbf{T}_N = \gamma_0\mathbf{1} + \gamma_1(\text{tr}\mathbf{D})\mathbf{1} + \gamma_2\mathbf{D} \quad (3.184)$$

where all scalar coefficients k , χ , γ_0 , γ_1 , γ_2 are (generally nonlinear) functions only of ρ and T . But in equilibrium (3.159) the nonequilibrium stress and heat flux must be zero (3.163), (3.170) at any ρ , T and \mathbf{h} and therefore in (3.183) and (3.184) the following coefficients are identically (i.e., for all ρ , T) zero³⁷

$$\chi \equiv 0 \quad (3.185)$$

$$\gamma_0 \equiv 0 \quad (3.186)$$

Therefore from (3.183) and (3.185) we obtain the *Fourier law* of heat conduction

$$\mathbf{q} = -k\mathbf{g} \quad (3.187)$$

³⁷ As we note at the end of Sect. 3.6 all this and the subsequent results follow if the assumption of linearity has been used in a constitutive relation of a nonsimple fluid with viscosity and heat conduction (3.127), (3.146) (i.e., before application of admissibility principle). These constitutive relations are scalar, vector and symmetric tensor isotropic functions (3.128) (including f) which are linear in vector \mathbf{g} , \mathbf{h} and symmetrical tensor \mathbf{D} .

The representation theorems for such linear functions (A.67), (A.58), (A.68) from Appendix A.2 then gives for scalar functions

$$s = s^{(0)} + s^{(1)}\text{tr}\mathbf{D}, \quad u = u^{(0)} + u^{(1)}\text{tr}\mathbf{D}$$

$$f = f^{(0)} + f^{(1)}\text{tr}\mathbf{D}$$

and (3.183) and (3.184) for vector and tensor functions. Similarly, as scalar coefficients here, the scalars $s^{(0)}$, $u^{(0)}$, $f^{(0)} \equiv u^{(0)} - Ts^{(0)}$, $s^{(1)}$, $u^{(1)}$, $f^{(1)} \equiv u^{(1)} - Ts^{(1)}$ are (generally nonlinear) functions of density ρ and temperature T . Using them in the reduced inequality (3.113) and by the admissibility principle, we obtain all the results (like (3.185), (3.186), etc.) of this section (namely $s^{(1)}$, $u^{(1)}$, $f^{(1)}$ are zeros identically), see [14, 27, 84].

where $k = \hat{k}(\rho, T)$ is the *heat conductivity* which is a function of ρ, T . Similarly from (3.186) and (3.184), using the divergenceless stretching tensor $\mathring{\mathbf{D}}$ defined as

$$\mathring{\mathbf{D}} \equiv \mathbf{D} - (1/3)\text{tr}\mathbf{D}\mathbf{1}, \quad \text{tr } \mathring{\mathbf{D}} = 0 \quad (3.188)$$

and with $\zeta \equiv \gamma_1 + (1/3)\gamma_2$, $\eta \equiv (1/2)\gamma_2$, we obtain the *Newton law of viscosity*

$$\mathbf{T}_N = \zeta(\text{tr}\mathbf{D})\mathbf{1} + 2\eta \mathring{\mathbf{D}} \quad (3.189)$$

where $\zeta = \hat{\zeta}(\rho, T)$ are the *volume (bulk) viscosity* and $\eta = \hat{\eta}(\rho, T)$ the (dynamical) *viscosity coefficients* respectively, both are (generally nonlinear) functions of ρ, T only. Note that $\text{tr}\mathbf{D}$ and $\mathring{\mathbf{D}}$ are mutually independent (choosing them arbitrarily and independently we obtain the corresponding \mathbf{D} according to (3.188)).

The other constitutive equations are the same as in Sect. 3.6 (cf. (3.175), (3.171), (3.173))

$$f = \hat{f}(\rho, T) \quad (3.190)$$

$$s = \hat{s}(\rho, T) \quad (3.191)$$

$$u = \hat{u}(\rho, T) \quad (3.192)$$

$$\frac{\partial \hat{f}}{\partial T} = -s \quad (3.193)$$

$$\rho^2 \frac{\partial \hat{f}}{\partial \rho} = P = \hat{P}(\rho, T) \quad (3.194)$$

$$\mathbf{T} = -P\mathbf{1} + \zeta(\text{tr}\mathbf{D})\mathbf{1} + 2\eta \mathring{\mathbf{D}} \quad (3.195)$$

where P, ζ, η are functions of ρ and T only. Production of entropy in the linear fluid follows from (3.178) inserting (3.187) and (3.189)

$$T\sigma = \zeta(\text{tr}\mathbf{D})^2 + 2\eta\text{tr}(\mathring{\mathbf{D}})^2 + T^{-1}k\mathbf{g}^2 \geq 0 \quad (3.196)$$

Because this quadratic form (of mutually independent variables) is positive semidefinite [85, 86], we obtain that the transport coefficients ζ, η, k are nonnegative for all ρ, T

$$\zeta \geq 0, \quad \eta \geq 0, \quad k \geq 0 \quad (3.197)$$

Equilibrium in the linear fluid will be thoroughly discussed in Sect. 3.8 in which we also confine this model to the *regular* one to avoid unusual situations or to achieve its stability (see (3.232)–(3.234), (3.256), (3.257), Rem. 42).

It is noteworthy that the independent variable \mathbf{h} is not present at all in this linear model; therefore we would obtain the same results by analogous linearization of simple fluid (3.129), cf. end of Sect. 3.6 [9, 23, 24, 45] (but the presence of density gradients will be important in mixtures, see Sect. 4.8).

At the end we stress several characteristic features of the linear fluid. Though the thermodynamic quantities f, u, s, P as well as the transport coefficients k, ζ, η are functions of ρ and T only, no relationships exist between these two groups. Therefore it is impossible to obtain transport coefficients from equilibrium measurements. But such measurements suffice to obtain the thermodynamic functions, because the *Gibbs equation* is valid (by (3.193), (3.194))

$$\dot{f} = -s\dot{T} + (P/\rho^2)\dot{\rho} = -s\dot{T} - P\dot{v} \quad (3.198)$$

where the *specific volume* v was introduced

$$v \equiv 1/\rho \quad (3.199)$$

(remember that the same symbol used in dv in integrals has a different meaning, cf. (3.21), (3.275)).

These and other thermodynamic relations below are written in classical thermodynamics with differentials instead of material derivatives, e.g. dT instead of \dot{T} , cf. Sect. 4.6. As may be seen from Sect. 3.1 also $\partial/\partial t$ or grad may be used here.

Again, the (principle of) *local equilibrium* (cf. end of Sect. 3.6) which was deduced by the method of rational thermodynamics for the linear model (results (3.198)–(3.209) is also valid for the more general model of nonlinear fluid of preceding Sect. 3.6; cf. (3.157), (3.155), (3.169) [24, 75, 77, 78]); however, the local equilibrium is not to be expected as generally valid (cf. Sects. 2.2, 2.3).

Other forms of the Gibbs equation are

$$\dot{u} = T\dot{s} + (P/\rho^2)\dot{\rho} = T\dot{s} - P\dot{v} \quad (3.200)$$

$$\dot{g} = -s\dot{T} + v\dot{P} \quad (3.201)$$

Here (3.111) and the specific *Gibbs energy* (*free enthalpy*) or (specific) *chemical potential* g defined as

$$g \equiv \frac{\partial \rho \hat{f}}{\partial \rho} \quad (3.202)$$

have been used. Then, by (3.194), (3.199), a more classical form of this definition may be seen as in

$$g = f + Pv \quad (3.203)$$

It is well known that chemical potentials play an important role in many, usually more complicated models in the description of phase and chemical equilibria in

mixtures (cf. Sects. 2.4, 2.5 and Chap. 4), surface phenomena, etc. Chemical potential may be generalized to more general material models (including, e.g. solids).³⁸

Often the inversion of the function (3.194) $P = \hat{P}(\rho, T)$ for ρ is used

$$\rho = \tilde{\rho}(T, P) \quad (3.204)$$

assuming $\frac{\partial \hat{P}}{\partial \rho} \neq 0$ for every temperature T , cf. (3.234). This is practically fulfilled out of phase changes because of the stability criterion $\frac{\partial \hat{P}}{\partial \rho} > 0$, see (3.257).

Then P, T may be used instead of ρ, T as independent variables, e.g.

$$g = \hat{g}(\rho, T) = \tilde{g}(T, P), \quad u = \tilde{u}(T, P), \quad s = \tilde{s}(T, P) \quad (3.205)$$

Comparing (3.205) with (3.201) we have

$$\frac{\partial \tilde{g}}{\partial T} = -s \quad (3.206)$$

$$\frac{\partial \tilde{g}}{\partial P} = v \quad (3.207)$$

and from (3.200), (3.204), (3.205)

$$\begin{aligned} \dot{s} &= (1/T)\dot{u} - (P/(T\rho^2))\dot{\rho} = (1/T) \left(\frac{\partial \tilde{u}}{\partial T} - (P/\rho^2) \frac{\partial \tilde{\rho}}{\partial T} \right) \dot{T} \\ &+ (1/T) \left(\frac{\partial \tilde{u}}{\partial P} - (P/\rho^2) \frac{\partial \tilde{\rho}}{\partial P} \right) \dot{P} \end{aligned} \quad (3.208)$$

From the last equation the form of derivatives $\tilde{s}(T, P)$ may be seen. Using them in the integrability condition $\partial^2 \tilde{s} / \partial P \partial T = \partial^2 \tilde{s} / \partial T \partial P$ we obtain after some calculation

$$\frac{\partial \tilde{u}}{\partial P} = (T/\rho^2) \frac{\partial \tilde{\rho}}{\partial T} + (P/\rho^2) \frac{\partial \tilde{\rho}}{\partial P} \quad (3.209)$$

³⁸ As the *configurational* or *material* forces [4, 87] (note that the density of chemical potential ρg has a pressure dimension). An analog of chemical potential is the *Eshelby tensor* (of chemical potential) $\underline{\Gamma}$ defined as $(\mathbf{F}^{-T} \equiv (\mathbf{F}^T)^{-1})$

$$\underline{\Gamma} \equiv f \mathbf{1} - (1/\rho) \mathbf{F}^T \mathbf{T} \mathbf{F}^{-T}$$

Note, that if stress is reduced to pressure P , $\mathbf{T} = -P \mathbf{1}$, (usual in fluids) this definition gives the classical result (3.203) $\underline{\Gamma} = g \mathbf{1}$, see (3.199). The Eshelby tensor, e.g. gives the condition of phase equilibria (Maxwell relation—equality of chemical potentials (2.116) in fluid phases), namely equality of $\underline{\Gamma} \mathbf{n}$ on both sides of equilibrated solid phases (\mathbf{n} is the normal to phase boundary) and may be also used to describe surface phenomena, dislocations, etc. [1, 4, 87]. Eshelby tensors may also be defined in mixtures [2, 3].

With (3.204) we can write the transport coefficients k , ζ , η (functions of ρ and T) also as functions of P , T

$$k = \tilde{k}(T, P), \quad \zeta = \tilde{\zeta}(T, P), \quad \eta = \tilde{\eta}(T, P) \quad (3.210)$$

We also note that the vector or tensor responses (3.187), (3.189) depend only on the vector or tensor “driving forces” respectively. This fact is known in linear irreversible thermodynamics as the “Curie principle” [36, 80, 88, 89] (cf. discussion in [34, 38]). Present theory shows however, that this property follows from the isotropy of constitutive functions and from the representation theorems of such linear functions, see Appendix A.2, Eqs. (A.11)–(A.13) and (A.57)–(A.59). But representation theorems for nonlinear isotropic constitutive functions [64, 65] show that the “Curie principle” is not valid generally.

In processes with $\mathbf{g} = \mathbf{o}$ and $\mathring{\mathbf{D}} = \mathbf{0}$ the nonequilibrium stress is reduced to the nonequilibrium pressure P_N

$$\mathbf{T}_N = -P_N \mathbf{1}, \quad \text{where} \quad P_N \equiv -\zeta \text{tr} \mathring{\mathbf{D}} = -\zeta(T, v) \frac{\dot{v}}{v} \quad (3.211)$$

where (3.189), (3.63), (3.16), (3.199) have been used. Such nonequilibrium pressure exists even in a uniform system which is in fact the uniform model B from Sect. 2.2 (see (2.34); volume V is proportional to v) with linear dependence on \dot{V} discussed in Rem. 8 in Chap. 2.

Recapitulating the results we need (from experiment or from molecular models) in this model of fluid

- (i) to describe their transport behaviour: the heat conductivity k , volume viscosity ζ and viscosity η and their dependences on temperature and density;
- (ii) to describe their thermodynamics: the *state equation* $P = \hat{P}(\rho, T)$ (3.194) and the *caloric state equation* $u = \hat{u}(\rho, T)$ (3.192). In fact, here we need the dependence on temperature only (usually in the form of dependence of heat capacity at constant volume) (see Appendix A.1, Rem. 5 in Appendix A) because dependence (3.192) on density may be calculated from the state equation (3.194) (namely, this gives, by interchangeability of mixed derivatives in (3.198), the dependence of s on density and therefore, by another form of Gibbs equation (3.200), the dependence of u on density).

In the simplest case of *ideal gas* (defined in Appendix A.1) the state (3.194) and caloric (3.192) equations are

$$P/\rho = Pv = (R/M)T \quad (3.212)$$

(see (A.3), (A.10) with use (3.199) and molar mass M) and (see Rems. 15 in Chap. 1, 5 in Appendix A)

$$u = \hat{u}(T) \quad (3.213)$$

As we explain in Appendix A.1 the experience shows that (3.212), (3.213) are valid for any gas in the limit of zero densities, even with nonlinear transport³⁹ and they were used for the definitions of absolute temperature and entropy (see (A.9), (1.28), (1.30), (1.31)).

Finally we can define the *incompressible* fluids which model *liquids* approximately because the dependence of liquids properties on the pressure may be neglected at nonextreme, say atmospheric, values of the pressure.

Incompressible fluids have been defined by mechanical internal constraint $J = 1$ in Rem. 5.3 but they may be defined (more specially and naturally) from previous thermodynamic formulae (3.204)–(3.209) neglecting their dependence on pressure [24]. Namely, we have by definition (instead of (3.204), (3.205))

$$\rho = \tilde{\rho}(T), \quad s = \tilde{s}(T), \quad u = \tilde{u}(T) \quad (3.214)$$

Then from integrability condition (3.209) it follows that density is independent of temperature

$$\rho \equiv \text{const.} \quad (3.215)$$

therefore density is a unique (positive) constant in this definition of incompressible fluid.

But then, by (3.16), (3.63), (3.65), we obtain

$$\text{div} \mathbf{v} = \text{tr} \mathbf{D} = 0, \quad J = 1 \quad (3.216)$$

which we have seen also in the mechanical definition. Note that even these formulae are valid for the linear fluid model and they are valid also in the nonlinear model from the previous Sect. 3.6 because thermodynamic formulae (3.204)–(3.209) are valid there too (cf. the discussion of local equilibrium above (3.200)).

Transport equations in the incompressible fluids are (see (3.187), (3.188), (3.195), (3.216))

$$\mathbf{q} = -k \mathbf{g} \quad (3.217)$$

$$\mathbf{T} = -P \mathbf{1} + 2\eta \mathbf{D} \quad (3.218)$$

where, by the definition of incompressible fluids, the thermal conductivity k and the viscosity η are functions of temperature only

$$k = \tilde{k}(T), \quad \eta = \tilde{\eta}(T) \quad (3.219)$$

³⁹ If we assume that the ideal gas studied fulfils the local equilibrium (and this is the usual case: ideal gas may be from the linear fluid models discussed here, but it may be also from some nonlinear models fulfilling this principle, e.g. those in [78]), then property (3.213) follows from state equation (3.212). Indeed, the local equilibrium means the validity of Gibbs equations (3.200)₁, (3.198)₁, from which $\partial \hat{u} / \partial \rho = T \partial \hat{s} / \partial \rho + P / \rho^2$ and $\partial \hat{s} / \partial \rho = -\partial(P / \rho^2) / \partial T$. By their combination and using state equation (3.212) we obtain identically $\partial \hat{u} / \partial \rho = 0$. Cf. also [27, Sect. 16], [90, 91].

and the pressure P is arbitrary scalar, cf. Rem. 26.

At the end we note that generalization of incompressibility on fluid mixtures is not straightforward, see Sect. 4.8.

Of course the results concerning nonlinear transport phenomena must be transformed correspondingly.

Summary. Section 3.7 derives the main model of interest in our book for the case of single fluid. This model of fluid with linear transport properties started with linearization of constitutive equations derived in preceding section for fluid vector and tensor quantities, i.e., for the heat flux and (nonequilibrium) stress tensor, taking into account that they are isotropic functions—see (3.183) and (3.184). Two classical laws immediately followed, viz. the Fourier law (3.187) and the Newton viscosity law (3.189). In the same time entropy inequality put some restrictions on the coefficients in these laws, cf. (3.197). It also followed that the Gibbs equation (3.198) is valid in this model and also the local equilibrium was proved. For our subsequent applications the definition of (specific) chemical potential (3.202) is important. Traditionally, the pressure is used as an independent variable in (chemical) thermodynamics. Though this was noted and used in paragraphs among Eqs. (3.204)–(3.210) the verification of this exchange of variables should be postponed to the next section. At the end the simplification to incompressible fluids is made which are defined by (3.214).

3.8 Equilibrium Processes in Linear Fluid

An *equilibrium process* in the linear fluid of Sect. 3.7 may be defined by (cf. (3.159))

$$\mathbf{D} = \mathbf{0} \quad (3.220)$$

$$\mathbf{g} = \mathbf{0} \quad (3.221)$$

because just these conditions give the zero entropy production

$$\sigma = 0 \quad (3.222)$$

as follows from (3.196), cf. discussion of (2.10), (2.11) and Rems. 12 in Chap. 1, 7 and 9 in Chap. 2.

Consider first an equilibrium process in the linear fluid model where (3.220), (3.221) are valid through all the body and persistently (at least for considered time interval); practically this is achieved by the *stability* discussed below [14, 18, 92–95].

The validity of (3.220) throughout the body is expressed by Killing's theorem (3.18), which is that the motion of a linear fluid body in an equilibrium process is rigid. This means that a frame fixed with such a body exists in which

$$\mathbf{v} = \mathbf{0} \quad (3.223)$$

through the body and persistently.⁴⁰ Such a frame, giving the zero velocity (3.223) in an equilibrium process, will be used in the following (among others it means that instead of material derivative we can use $\partial/\partial t$ in this frame). By persistence of (3.223) we have also

$$\dot{\mathbf{v}} = \mathbf{0} \quad (3.224)$$

through the body and persistently.

Constitutive equations (3.195), (3.188), (3.187) in such an equilibrium process are

$$\mathbf{T} = -P\mathbf{1} \quad (3.225)$$

$$\mathbf{q} = \mathbf{0} \quad (3.226)$$

With those equations the following forms of balances (3.63), (3.85), (3.107), (3.109) are valid ((3.93) is trivially satisfied)

$$\dot{\rho} = 0 \quad (3.227)$$

$$\text{grad}P = \rho(\mathbf{b} + \mathbf{i}) \quad (3.228)$$

$$\rho\dot{u} = Q \quad (3.229)$$

$$\rho\dot{s} = Q/T \quad (3.230)$$

The persistence and validity of these equations through the body therefore give the behaviour of other formulae such as $\frac{\partial\rho}{\partial t} = 0$, $\frac{\partial\mathbf{g}}{\partial t} = \mathbf{0}$, $\frac{\partial\mathbf{h}}{\partial t} = \mathbf{0}$, etc.

Now, we restrict ourselves to some equilibrium process persisting in one equilibrium state of the linear fluid model in the sense of the property S4 from Sect. 1.2 (one equilibrium from those more possible which is compatible with the given boundary and external conditions).⁴¹ Such an equilibrium state may be achieved if no radiation heat transfer is considered

$$Q = 0 \quad (3.231)$$

⁴⁰ Cf. (3.18), Rem. 5 and deduction of (3.25). Because the change of frame describes the change of frame in a rigid motion to another one the result (3.223) is intuitively clear. Formally, inserting rigid motion from Rem. 5 into (3.25) we seek the (starred) frame in which $\mathbf{x}^* = \mathbf{X}$ (and therefore $\mathbf{v}^* = \mathbf{0}$, i.e., (3.223)) through the body. It may be seen that this need the change of frame by time functions $\mathbf{Q} = \underline{\Theta}^T$ and $\mathbf{c} = -\underline{\Theta}^T\boldsymbol{\gamma}$.

⁴¹ Note that an equilibrium process (as the time succession of states with (3.220)–(3.222)) with nonzero radiation $Q \neq 0$, which is even reversible, is possible: in the “straight” part of the process the heating (defined by the first two members on the right-hand side of (3.97)) is given as $\int_V Q \, dv$ by (3.226) (V is the volume of the body); see also

Moreover we add to the linear fluid model the following *regularity* conditions⁴² valid at any ρ, T , i.e., at any state, not only in the equilibrium one:

Transport coefficients are always positive (as different from (3.197))

$$\zeta > 0, \quad \eta > 0, \quad k > 0 \quad (3.232)$$

and the following derivatives are nonzero

$$\frac{\partial \hat{u}}{\partial T} \neq 0 \quad (3.233)$$

$$\frac{\partial \hat{P}}{\partial \rho} \neq 0 \quad (3.234)$$

at any T, ρ .

Therefore, in this section, we study the *regular linear fluid body* or the *fluid with linear transport properties with regular responses* consisting of the linear fluid body of Sect. 3.7 to which we add the regularity properties (3.232)–(3.234).

In such *regular linear fluid* with no radiation (3.231) we define the *equilibrium* or *equilibrium state* by the zero entropy production (3.222) which is valid through all the body and persistently.

(Footnote 41 continued)

Sect. 1.2, models A, B in Sect. 2.2 and Rems. 12 in Chap. 1, 48 in this chapter.

Temperature may change in time but not in space (3.221) during such an equilibrium process in the rigid and not moving body, density does not change in time (3.227) (but may change in space); u, s change as the temperature changes, similarly P changes by a corresponding time change of $\mathbf{b} + \mathbf{i}$ (say by (3.192), (3.191), (3.194) in the linear fluid model). The reverse process may be imagined to exist as going through the same states of the equilibrium process, power and entropy production are again zero, heating is of reverse sign $-\int_V Q dv$ (in comparison with the appropriate instant of “straight” equilibrium process).

Even this reversible process is rather a special one. We note it here to demonstrate that in the model of the linear fluid equality (in entropic inequality) is possible, see (1.35), and to show that entropy may be calculated with the precision of a constant, see (1.40), cf. application of reversible processes in Sect. 1.4. An equilibrium state is also an equilibrium process formed by a unique state with (3.231), cf. definition below (2.11).

⁴² Similarly as in Rem. 11 in Chap. 1 and in Sects. 2.1, 2.2, we try to avoid in this way the unusual, often “pathological” situations of real complex materials in our simple models (as, e.g. zero values of some transport coefficients (3.197) at certain ρ, T); other motivation is the “practical realization of the persistence of the equilibrium state” which may be achieved through its stability (discussed below), e.g. regularity conditions (3.233), (3.234) are even intensified in such a stable equilibrium state (both derivatives are positive, see (3.256), (3.257) below).

Again we assume that the constitutive model together with regularities introduced is valid in all situations, e.g. the model of fluid with linear transport properties with regular response is assumed to be valid for all values of ρ, T . Namely, we study the (properties of) model even though we know that there are values of ρ, T for which a real fluid does not fulfil some regularities assumed (e.g. stability in the region of phase transformations); as usually, such difficulties are resolved by the appropriate limiting applications of the model studied.

Then “equilibrium conditions” (3.220), (3.221) are valid through the body and persistently because the quadratic form (3.196) is positive definite due to regularity conditions (3.232)⁴³ and, reversely, from (3.220), (3.221) equation (3.222) follows.

Therefore (3.225)–(3.228) are valid and, by (3.229)–(3.231), we have

$$\dot{\mathbf{u}} = 0 \quad (3.235)$$

$$\dot{\mathbf{s}} = 0 \quad (3.236)$$

From (3.235), (3.192), (3.227), and regularity (3.233) we have through the body and persistently

$$\dot{T} = 0, \text{ or by (3.223) } \frac{\partial T}{\partial t} = 0 \quad (3.237)$$

This, together with (3.221), means that a unique and constant (in time) temperature is everywhere in the body in this equilibrium (note that, reversely, Eq. (3.231) follows from (3.237), cf. (3.192), (3.227), (3.229) [76]).

Inserting constitutive equation for P (3.194) into (3.228) and using (3.221) we have

$$\frac{\partial \hat{P}}{\partial \rho} \mathbf{h} = \rho(\mathbf{b} + \mathbf{i}) \quad (3.238)$$

and making another time derivative of this equation (using zero time derivatives of ρ , \mathbf{h} , T) we obtain $\partial(\mathbf{b} + \mathbf{i})/\partial t = \mathbf{o}$, i.e., the body and/or inertial force must be constant in time in such an equilibrium process. Further, from (3.238), it follows that $\mathbf{h} \neq \mathbf{o}$ because of (3.234); in the special case $\mathbf{b} + \mathbf{i} = \mathbf{o}$ (no body and/or inertial forces), density gradient disappears $\mathbf{h} = \mathbf{o}$.

Therefore we can conclude that during such equilibrium process in the frame with persisting and everywhere zero velocity (3.223), the body is in one “persisting” equilibrium state in the sense of Sect. 1.2 in which density does not change in time but may change in space (if the body or inertial forces are nonzero constants in time), while temperature is everywhere the same persistent constant. Heating and power (the right-hand side of energy balances), e.g. of (3.103), (3.106) or (3.107) are zero (see (3.226), (3.231), (3.220), (3.223)) and in such an equilibrium state also all responses in the particles of the body do not change in time (cf. (3.227), (3.237), (3.225), (3.194)) but some of them (the density and properties depending on the density) may have nonzero space gradients (parallel to the time constant nonzero body and/or inertial forces; cf. (3.238), (3.221), (3.192)); temperature is a unique constant in all body.

⁴³ Calculation of $\text{tr}(\overset{\circ}{\mathbf{D}})^2$ in (3.196) gives $\text{tr}(\overset{\circ}{\mathbf{D}})^2 = (D^{11})^2 + (D^{22})^2 + (D^{33})^2 + 2(D^{12})^2 + 2(D^{13})^2 + 2(D^{23})^2$ and therefore zero entropy production (3.222) and positivity (3.232) give from (3.196) the result (3.221) as well as $\text{tr} \overset{\circ}{\mathbf{D}} = 0$ and $D^{11} = D^{22} = D^{33} = D^{12} = D^{13} = D^{23} = 0$ which with definition (3.188) of $\overset{\circ}{\mathbf{D}}$ gives (3.220).

The body force having a potential Φ is of practical importance; the potential, similarly as with this force, must be constant in time (3.104). In this case the chemical potential (3.205)–(3.207) is preferred (note use of regularity (3.234) here) because, by (3.221), (3.199), $\text{grad}g = (1/\rho)\text{grad}P$ and therefore the equilibrium result (3.228) with time constant potential Φ (3.104) may be written as

$$\text{grad}(g + \Phi) = \mathbf{o} \quad (3.239)$$

in such an equilibrium state.⁴⁴ Probably the most important is this equilibrium in an inertial frame without the body force ($\mathbf{i} = \mathbf{o}$, $\mathbf{b} = \mathbf{o}$) because then space gradients disappear as we noted above and we obtain a *uniform equilibrium* state, not changing in time which, in fact, was exemplified by the uniform model A or by equilibrium in the model B of Sects. 2.1, 2.2, see also below.

Time persistence of an equilibrium state through the persistence of its conditions (like (3.220), (3.221), (3.227), (3.237)) may be realized in practice with great difficulties (or it is even impossible) because of molecular fluctuations. The practical persistence of an equilibrium state (and therefore also the assumption S4 in Sect. 1.2) may be achieved by its *stability* and this is analyzed in the rest of this section; we are inspired mainly by [1, 18, 92, 93], see also [94, 95, 97–102].

We concentrate here on the stability of our model of regular linear fluid (giving the classical Gibbs stability) modelling one-phase fluid.⁴⁵ We try to find such properties of constitutive equations which permit to realize equilibrium states in our model at some ρ , T (and also motivate some of the regularity conditions above). If such stability properties are not fulfilled then, typically, our (one-phase) fluid system disintegrates into more phases, cf. Rem. 45.

The *stability* of equilibrium state may be roughly defined as gradual return to the equilibrium after some disturbance from this state at fixed boundary and exterior conditions of the body. The mere removal of such disturbances (caused by molecular nature of studied material) causes the real persistence of the equilibrium state. As noted above, this property need not be valid generally in real material and depends on its formulation. Here we discuss sufficiently general stability of an isolated body resulting from the classical Gibbs stability [93–95, 97] which permits to obtain additional regularity properties—the *conditions of stability* of constitutive equations of our fluid model. Namely, consider an isolated body modelled by the linear fluid (3.187)–(3.196) with regular response (3.232)–(3.234) which is in an equilibrium

⁴⁴ This result (3.239) may be generalized for Eshelby tensor $\underline{\Gamma}$ (generalization of chemical potential, e.g. for solids, see Rem. 38) as

$$\text{Div}(\underline{\Gamma} + \Phi\mathbf{1}) = \mathbf{o}$$

cf. [1, 96] (Div is the divergence in referential description).

⁴⁵ But we omit the generalizations of equilibrium stabilities for phase transitions [1, 103–106] (for them typically criteria stability like (3.256), (3.257) are not valid), for more general materials (say solids), and the more complicated problem of stability of nonequilibrium states (e.g. the vast field of dissipative structures [24, 37, 80, 107–109]) because most of these issues do not concern our (one-phase) model or are now in the stage of intensive and not completely resolved research; see also Rem. 31 in Chap. 4.

state defined by (3.222) (or by (3.220), (3.221)) the persistence of which is achieved by the zero body heating (3.231), the zero inertial and body forces ($\mathbf{i} = \mathbf{o}$, $\mathbf{b} = \mathbf{o}$) and the zero velocity $\mathbf{v} = \mathbf{o}$ (3.223) everywhere. The body is in the uniform equilibrium state mentioned above and as may be seen, such a state may be realized in the *isolated* body in which no exchange of heat, work and mass with environment exists and the boundary of which is fixed. Denoting constant (throughout the body and time) equilibrium values of temperature T^o density ρ^o and therefore also specific volume v^o , internal energy u^o and entropy s^o (cf. (3.191), (3.192), (3.199)) we can express the volume V^o , energy E^o and entropy S^o of the body in such equilibrium by

$$V^o = v^o m^o \quad (3.240)$$

$$E^o = u^o m^o \quad (3.241)$$

$$S^o = s^o m^o \quad (3.242)$$

where m^o is the mass of the body.

We say that such a uniform equilibrium state is *dynamically stable under isolation*, if an arbitrary “perturbed” state of the body compatible with isolation decays back to this equilibrium state. *Compatibility with isolation* means that during the whole return to the equilibrium state the energy and the volume is the same as in the original equilibrium state, E^o , V^o , further $\mathbf{b} = \mathbf{o}$, $Q = 0$ through the body and $\mathbf{v} = \mathbf{o}$, $\mathbf{q} = \mathbf{o}$ on the boundary (but generally nonzero inside the body). Therefore in an arbitrary state during this return (and including the original perturbed state as well) we have by (3.21) (with the density ρ and $dm = \rho dv$; cf. (3.199)), using the specific volume v , total energy and entropy and integrating through mass m^o of the body,

$$V^o = \int_{m^o} v dm \quad (3.243)$$

$$E^o = \int_{m^o} \left(u + \frac{1}{2} \mathbf{v}^2 \right) dm \quad (3.244)$$

while the entropy S of an arbitrary state grows up (see (3.108)) to its maximum value S^o (3.242)

$$S = \int_{m^o} s dm \leq S^o \quad (3.245)$$

i.e., in accord with the regular equilibrium response, we can conclude that the equality in (3.245) is valid only for a uniform equilibrium state (the stability of which is tested).

In fact, by the assertion that this equilibrium state is dynamically stable under isolation, we express an extra *postulate* that the state compatible with isolation and with the entropy S comes back to the equilibrium state with the entropy value S^o (3.242) in this isolated system.

This postulate is in agreement with traditional and reasonable expectation of achieving finite extremal values of entropy in a process occurring in an isolated system (an increase of entropy only follows from inequality (3.108)). Similarly, finite extremal values of other potentials at corresponding conditions, like the minimum of (say Gibbs) energies, etc., may be expected cf. [1, 37, 92, 110, 111].

In what follows we deduce the conditions of stability (3.256), (3.257) from this postulate. Then, in the remaining part of this section following mainly [18, 93], we try, on the contrary, to show that the stability conditions in the regular linear fluid lead to this postulate, see (3.266).

Result (3.245) is valid for any perturbed state and therefore also for such a state with zero velocity inside the body; then, instead of (3.244), we have in that perturbed state

$$E^o = \int_{m^o} u \, dm \quad (3.246)$$

with volume and entropy given again by (3.243), (3.245) (in the following states of a body when approaching the equilibrium state the velocity need not be zero inside although it must be zero at the boundary). This special case of any perturbation with (3.243) and (3.246) (instead of (3.244)), considering (3.245), is in fact the classical definition of the *Gibbs stability* under isolation [92, 93]. Although the Gibbs stability is studied in classical thermodynamics with uniform model (like A of Sect. 2.2), its dynamical interpretation [18, 93, 97, 106] cannot be described in terms of such a uniform model, namely a nonuniform perturbed state permitting the nonequilibrium processes and therefore inequalities in (3.245) must be possible (in fact this is more or less explicitly expressed in classical proofs, see, e.g. [112, p. 82, Sect. 21]). This motivates the following procedure [93]:

Assume that a given uniform equilibrium state of the linear fluid with regular equilibrium response is dynamically stable under isolation. Therefore it is also Gibbs stable (namely its starting perturbed state may have zero velocity inside and (3.246) is valid). This suffices for the following result: the function

$$s = \bar{s}(u, v) \quad (3.247)$$

is *strict concave* in the corresponding domain (such function (3.247)⁴⁶ follows from (3.191) inserting inversion of (3.192) for T (which exists by (3.233)) and using (3.199)).

Indeed, let us choose a perturbed state with zero velocity inside in the following way: we divide the body on two parts with masses αm^o and $(1 - \alpha)m^o$ where $0 < \alpha < 1$; internal energies u^a, u^b and specific volumes v^a, v^b ($u^a \neq u^b, v^a \neq v^b$) are constant (uniform) but different in these parts and entropies s^a, s^b are given by

⁴⁶ It follows from our intention to use the theorem of concave function from Appendix A.3 for the proof. This assumes the negative (or positive) definiteness of a matrix composed from second derivatives of such a function. This property has, besides (3.247), e.g. function $\bar{g}(T, P)$ (3.205) (used also below in this section) but unfortunately not the more natural $\hat{f}(\rho, T)$ (3.190) or even $\check{f}(v, T)$ (see (3.199)); cf. [113, Sect. 39].

(3.247). Because of the compatibility with isolation of that perturbed state we have by (3.243), (3.246), (3.240), (3.241)

$$v^a \alpha m^o + v^b (1 - \alpha) m^o = V^o, \quad u^a \alpha m^o + u^b (1 - \alpha) m^o = E^o \quad (3.248)$$

Inserting (3.240), (3.241) and removing m^o we obtain

$$v^a \alpha + v^b (1 - \alpha) = v^o, \quad u^a \alpha + u^b (1 - \alpha) = u^o \quad (3.249)$$

But using such a perturbed state in (3.245)

$$s^a \alpha m^o + s^b (1 - \alpha) m^o < S^o \quad (3.250)$$

(equality disappears because of the nonuniformity of the perturbed state; cf. (3.245)). By (3.242), (3.247) we have

$$\alpha \bar{s}(u^a, v^a) + (1 - \alpha) \bar{s}(u^b, v^b) < \bar{s}(u^o, v^o) \quad (3.251)$$

By definition (i) in the theorem of concave functions (Appendix A.3), the function (3.247) is strict concave (see (A.70), (A.71), (A.72), (3.247), (3.249), (3.251) with $\bar{\omega} = (u, v)$ and $\Gamma = s$). Therefore property (iii) of this theorem is equivalently valid for function (3.247): the matrix of its second derivatives is negative definite at all corresponding u, v , i.e.,

$$\frac{\partial^2 \bar{s}}{\partial u^2} = -\left(T^2 \frac{\partial \hat{u}}{\partial T}\right)^{-1} < 0 \quad (3.252)$$

$$\frac{\partial^2 \bar{s}}{\partial u^2} \frac{\partial^2 \bar{s}}{\partial v^2} - \left(\frac{\partial^2 \bar{s}}{\partial u \partial v}\right)^2 = \frac{\partial(T, \rho)}{\partial(u, v)} \frac{\partial(T^{-1}, PT^{-1})}{\partial(T, \rho)} = \frac{\rho^2}{T^3} \frac{\partial \hat{P}}{\partial \rho} \left(\frac{\partial \hat{u}}{\partial T}\right)^{-1} > 0 \quad (3.253)$$

Here we use the properties of the negative definite matrix and Jacobians [85, 86], (3.192), (3.194) and (as follows from (3.200))

$$\frac{\partial \bar{s}}{\partial u} = \frac{1}{T} \quad (3.254)$$

$$\frac{\partial \bar{s}}{\partial v} = \frac{P}{T} \quad (3.255)$$

Thus it follows from (3.252), (3.253) (because $T > 0, \rho > 0$) that if the linear fluid body with regular equilibrium response is dynamically stable (or Gibbs stable) under isolation then at each corresponding T, ρ the following *stability conditions* are valid

$$\frac{\partial \hat{u}}{\partial T} > 0 \quad (3.256)$$

$$\frac{\partial \hat{P}}{\partial \rho} > 0 \quad (3.257)$$

in our models. In what follows we use these conditions (3.256), (3.257) instead of (3.233), (3.234) as regular conditions (besides (3.232)) to our model of fluid with linear transport properties because, as we shall show in the rest of this section, such models then have dynamical stability not only under isolation but even at other conditions.

It has been shown that results (3.256), (3.257) are necessary for dynamical stability of our linear fluid of Sect. 3.7 (with regularity (3.232)).

Now we try to prove also the sufficiency: assuming stability conditions (3.256), (3.257) we try to show that the body of regular linear fluid of Sect. 3.7 (with further regularities (3.232)), kept permanently in isolation (defined below) develops asymptotically to uniform equilibrium state. That is we prove the dynamical stability under isolation (and also Gibbs stability) for such a body. But the time behaviour of the perturbed system is generally a very complicated task—we need to solve the system of differential equations obtained by substitution of constitutive equations into balances.

For simplicity therefore we show only that the uniform equilibrium state (those given by (3.240)–(3.242)) is the possible one in which the perturbed state kept permanently in isolation (defined below) develops asymptotically as time goes to infinity [1, 18, 93, 97].

Let us have some perturbed state of a body made from the linear fluid (3.187)–(3.196) with regular equilibrium response ((3.232) is valid) and with stability conditions (3.256), (3.257), which is held permanently in an inertial frame without body force in isolation (no heat, work and mass exchange with surroundings). That is we have persistently through the body $\mathbf{i} = \mathbf{o}$ (3.48), $\mathbf{b} = \mathbf{o}$, no heat radiation $Q = 0$ (3.231) and on its boundary no heat exchange $\mathbf{q} = \mathbf{o}$ and zero velocity $\mathbf{v} = \mathbf{o}$.

Therefore the body, having permanently constant mass m^o , volume V^o and energy E^o given by (3.243), (3.244) with corresponding local specific volume v and energy u of the given state, develops asymptotically to a uniform equilibrium state with specific internal energy u^o and volume v^o given by

$$u^o \equiv E^o / m^o \quad (3.258)$$

$$v^o \equiv V^o / m^o \quad (3.259)$$

Because of assumed stability conditions (3.256), (3.257) we achieve from (3.252), (3.253) the fulfilment of property (iii) from Appendix A.3 for function (3.247). Therefore equivalently (A.73) is valid for this function (3.247), giving s^o for values u^o , v^o (3.258), (3.259) and s for values u , v in any place of the body in arbitrary state during the process, i.e.,

$$s < s^o + (1/T^o)(u - u^o) + (P^o/T^o)(v - v^o) \quad (3.260)$$

where T^o , P^o are values given by (3.254), (3.255). Equality in (3.260) is valid as

$$s = s^o \quad (3.261)$$

when (cf. in (A.73))

$$u = u^o \quad (3.262)$$

$$v = v^o \quad (3.263)$$

Now we add to the right-hand side of (3.260) the nonnegative quantity $(2T^o)^{-1} \mathbf{v}^2$ (with \mathbf{v} in the same place and instant as in (3.260)) and integrate such inequality through the body at some instant; using (3.243), (3.244), (3.258), (3.259) we have

$$S(t) \equiv \int_{m^o} s \, dm \leq \int_{m^o} s^o \, dm \equiv S^o = s^o m^o \quad (3.264)$$

where the equality sign in the middle occurs if the system is a uniform one ((3.261)–(3.263) are valid in any place of the body; this is the final state with entropy S^o , see above (3.266)).

Before going further we note that result (3.264) for a special perturbed state with (3.243), (3.246) (i.e., (3.244) with zero velocity through the body) expresses the Gibbs stability of a uniform state with U^o , V^o , S^o (3.258), (3.259), (3.264), deduced from the stability conditions (3.256), (3.257).

Turning back to dynamical stability we can see from entropy inequality (3.110) and (3.68) in this isolation (3.226), (3.231) that at any moment t during the development

$$\dot{S}(t) \equiv \overline{\int_{m^o} \dot{s} \, dm} = \int_{V^o} \sigma \, dv \geq 0 \quad (3.265)$$

Therefore, during the process, the entropy function $S(t)$ has two properties: it does not decrease in time (3.265) and has the upper limit S^o (3.264) (in this connection $S(t)$ is called a *canonical function*). We add a simplifying (and in fact expected) assumption that whenever inequality in (3.264) is valid, the inequality in (3.265) is valid too (cf. [93, Rem. 4.5, Theor. 3]). Then in uniform equilibrium achieved at $t \rightarrow \infty$ entropy reaches the value S^o from (3.264)

$$\lim_{t \rightarrow \infty} S(t) = S^o \quad (3.266)$$

cf. [93, Eq. (4.40)].

Assuming also that $\lim_{t \rightarrow \infty} \dot{S}(t)$ exists it cannot be positive because of the upper limit S^o (3.264) and therefore by (3.265)

$$\lim_{t \rightarrow \infty} \dot{S}(t) = 0 \quad (3.267)$$

Moreover, motivated by (3.265), we assume that this limit (3.267) may be written as $\lim_{t \rightarrow \infty} \dot{S}(t) = \int_{V^o} \sigma^o dv$ where σ^o are limits of (local) nonnegative entropy productions σ .

To localize these results we simply assume that all deductions may be repeated with any part of the considered body, i.e., with the corresponding part of mass, volume and other extensive quantities. Then result (3.267) may be written locally

$$\sigma^o = \lim_{t \rightarrow \infty} \sigma = 0 \quad (3.268)$$

in any place through the body.⁴⁷

Therefore at $t \rightarrow \infty$ the body achieves the state where there is zero entropy production $\sigma = \sigma^o = 0$ (3.222) in any place and permanently, and this is the equilibrium state defined with (3.240)–(3.242). In our linear fluid with regularity (3.232) we obtain from (3.196) (cf. Rem. 43) everywhere and permanently $\mathbf{D} = \mathbf{0}$ (3.220) and $\mathbf{g} = \mathbf{0}$ (3.221). Because of assumed zero velocity on the boundary of this equilibrium body, this rigid motion (3.18) gives zero velocity $\mathbf{v} = \mathbf{0}$ (3.223) everywhere and permanently inside. Constitutive equations (3.187), (3.195) give in this asymptotically equilibrium body (3.225), (3.226) and momentum balance (3.78) is then $\text{grad} P = (\partial \hat{P} / \partial \rho) \mathbf{h} = \mathbf{0}$. By (3.257) we obtain $\mathbf{h} = \mathbf{0}$ and by mass balance (3.227), we can see that the density (and therefore also the specific volume v^o following from (3.259) because of the constant volume V^o) in this equilibrium body is everywhere and permanently constant, as is similarly temperature. The latter follows by (3.221) and (3.237) which is given by energy balance (3.235) at $Q = 0$ (3.231). From this and similarly from the entropy balance (3.236) and also from (3.192), (3.191) results that also the specific internal energy and entropy are everywhere and permanently constant with values u^o (following from constant energy E^o in (3.258)) and s^o obtainable then from (3.247), cf. (3.261).

Admitting the results (3.266), (3.268), the conditions (3.256), (3.257) are sufficient for the dynamical stability of a uniform equilibrium state compatible with isolation for a linear fluid body with regular equilibrium response.

Similarly as with classical Gibbs stability it may be shown that the stability conditions lead analogously to dynamical stability at other conditions. As another example of such a kind we discuss the fluid body of a constant volume immersed in a thermostat and in a body force field (and, also without it as special case). We use again the method similar to those giving (3.266), see also [94, 95] and Sect. 4.7.

⁴⁷ Although assumptions giving (3.267), (3.268) look natural, this is not so, e.g. such $S(t)$ fulfilling (3.264), (3.265) may exist where $\dot{S}(t) > 0$ changes oscillatorily for any time and therefore a limit does not exist. Similarly the existence of limit (3.268) is not clear, e.g. σ^o in (3.267) may be nonzero on surfaces or lines (sets of zero measure) and such a situation may be obtained even by limitation from smooth function σ .

However, these difficulties may be avoided by other means, e.g. it is possible to prove (often with special types of material or with other potentials instead of entropy) the dynamical stability (even asymptotical one) but mostly in integral form (deviations are expressed by integral through the body). For further discussions see [1, 18, 93–95, 97–103, 114, 115].

Let us have a body consisting of linear fluid (of Sect. 3.7) with regular equilibrium response (3.232) with stability conditions (3.256), (3.257). The thermostatic boundary of this body has everywhere the same temperature T^o constant in time (the temperature inside the body may be arbitrary) and the boundary is fixed with $\mathbf{v} = \mathbf{o}$; therefore the volume of the body V^o is a constant. Heat may be exchanged but not by radiation, i.e., $Q = 0$ (3.231) through the body is valid. The mass of the body m^o is a constant which is independent of time

$$\int_{V^o} \rho \, dv = m^o \quad (3.269)$$

The body is situated in the body force field \mathbf{b} constant in time (e.g. earth gravitation), having the potential Φ

$$\mathbf{b} = -\text{grad}\Phi \quad (3.270)$$

$$\frac{\partial \Phi}{\partial t} = 0, \text{ i.e. } \Phi = \Phi(\mathbf{x}) \quad (3.271)$$

but the frame is inertial, $\dot{\mathbf{i}} = \mathbf{o}$ (cf. (3.104)).

We intend to show that a perturbed state compatible with these conditions may develop in $t \rightarrow \infty$ to the state which is in fact the *equilibrium* one: It has constant T^o and $\mathbf{v} = \mathbf{o}$ throughout the body, the stationary (equilibrium) pressure $P^o(\mathbf{x})$ is obtained by solution of (equilibrium) equation (3.228), (3.270)

$$\text{grad}P^o(\mathbf{x}) = -\rho^o(\mathbf{x}) \text{grad}\Phi(\mathbf{x}) \quad (3.272)$$

with stationary (equilibrium) density field $\rho^o(\mathbf{x}) \equiv \tilde{\rho}(T^o, P^o(\mathbf{x}))$. Such solution contains only one constant—pressure at one equipotential surface and this may be determined with the help of the known mass of the body (3.269) $m^o = \int_{V^o} \rho^o(\mathbf{x}) \, dv$.

The balance of energy for such a body follows from (3.105)

$$\overline{\int_{V^o} \rho(u + \frac{1}{2}\mathbf{v}^2 + \Phi) \, dv} = - \int_{\partial V^o} \mathbf{q} \cdot \mathbf{n} \, da \quad (3.273)$$

where ∂V^o is the boundary of the body with fixed volume V^o . Because temperature T^o is a constant we can eliminate the surface integral from (3.273) using entropy inequality (3.108) (with the help of entropy production σ (3.109) and (3.68), (3.23)) for such a body with (3.231). After rearrangements we obtain

$$\begin{aligned} - \int_{\partial V^o} \mathbf{q} \cdot \mathbf{n} \, da - \overline{\int_{V^o} \rho T^o s \, dv} &= \overline{\int_{V^o} \rho(u - T^o s + \frac{1}{2}\mathbf{v}^2 + \Phi) \, dv} \\ &= -T^o \int_{V^o} \sigma \, dv \leq 0 \end{aligned} \quad (3.274)$$

Because field $P^o(\mathbf{x})$ and V^o are time independent we have (by (3.199) and below)

$$0 = \frac{d}{dt} \int_{V^o} P^o dv = \frac{d}{dt} \int_{V^o} \rho v P^o dv \quad (3.275)$$

Using the Reynolds theorem (3.24) in (3.275) for $\mathbf{v} = \mathbf{o}$ on the boundary and adding this to (3.274) we obtain (the volume V^o is fixed, the dot over the integral and $\frac{d}{dt}$ have the same meaning)

$$\dot{R}(t) = -T^o \int_{V^o} \sigma dv \leq 0 \quad (3.276)$$

where the *canonical function* $R(t)$ is defined by

$$R(t) \equiv \int_{V^o} \rho(u - T^o s + P^o v + \frac{1}{2} \mathbf{v}^2 + \Phi) dv \quad (3.277)$$

Because of conditions of stability (3.256), (3.257) we obtain again the inequality (3.260) ($u \neq u^o, s \neq s^o, v \neq v^o; T^o > 0$, using again (A.73) from Appendix A.3 for function (3.247)). This may be written as

$$u - sT^o + vP^o > u^o - s^oT^o + v^oP^o \equiv g^o \quad (3.278)$$

where (cf. (3.191), (3.192), (3.199), (3.111), (3.203)) we can choose u^o, s^o, v^o, g^o as the values at $T^o, \rho^o(\mathbf{x}) \equiv \tilde{\rho}(T^o, P^o(\mathbf{x}))$ in the given place \mathbf{x} (calculated from (3.272)) and u, s, v are values at T, ρ in this place and some instant. Adding nonnegative quantity $\frac{1}{2} \mathbf{v}^2$ (the velocity is taken at this place and instant) to the left-hand side of (3.278) and adding the potential Φ to both sides, multiplying then the resulting inequality by $\rho > 0$ at this place and instant and integrating over the fixed volume V^o of the body in the given instant, we obtain

$$R(t) \geq R^o \quad (3.279)$$

(the equality is valid if $T = T^o, \rho = \rho^o, \mathbf{v} = \mathbf{o}$ through the body). Here the definition of canonical function (3.277) was used and R^o is defined by

$$R^o \equiv \int_{V^o} \rho(g^o + \Phi) dv = (g^o + \Phi)m^o \quad (3.280)$$

The right-hand side of (3.280) and therefore R^o is constant; indeed, $g^o(\mathbf{x}) = \tilde{g}(P^o(\mathbf{x}), T^o)$, (3.278) was obtained using the solution $P^o(\mathbf{x})$ of (3.272) and therefore (remember that for time-constant potential Φ the equilibrium relation (3.239) is valid) $g^o + \Phi$ is constant as well as the mass (3.269).

Therefore we constructed the canonical function (3.277) which does not increase (3.276) and which has a lower bound (3.279). Using a similar simplifying assumption as at (3.266), namely, whenever the inequality in (3.279) is valid, the inequality in (3.276) is valid too (cf. [93, Rem. 4.5, Theor. 3]), we obtain

$$\lim_{t \rightarrow \infty} R(t) = R^o \quad (3.281)$$

i.e., the time limit of canonical function $R(t)$ achieves value R^o . Therefore this regular linear fluid achieves asymptotically the equilibrium state with constant temperature T^o and no movement inside $\mathbf{v} = \mathbf{o}$ (3.223) (such were permanent on the boundary). This is the equilibrium with equilibrium pressure $P^o(\mathbf{x})$ and density $\rho^o(\mathbf{x})$ fields given by (3.272). Adding similar simplifying assumptions leading to (3.267), (3.268), we obtain, in this equilibrium, e.g. the result (3.268) in such a nonuniform body.

The dynamical stability just described contains as a special case the zero body force $\mathbf{b} = \mathbf{o}$ (again $\mathbf{i} = \mathbf{o}$) which leads to a final uniform equilibrium state (noted below (3.239)) without potential (say $\Phi = 0$).

The stability conditions (3.256), (3.257) lead analogously to stability at further conditions, e.g. the stability of a fluid in a thermostatic cylinder closed by a piston under constant pressure, cf. [14, 95, 97]. This may be done similarly as for mixtures in the last example of Sect. 4.7.

The processes going asymptotically to equilibrium discussed in this section may be used for understanding the reversible equilibrium processes as those processes which pass so slowly that the entropy production in (3.265), (3.276) may be neglected, cf. Sects. 1.2, 2.1, 2.2, in models A, B, Rems. 12 in Chap. 1, 7 and 9 in Chap. 2, 41 in this chapter and [116] (for simplicity we use linear model of Sect. 3.7).⁴⁸

Summary. This section shows the analysis of equilibrium state for a given system (single linear fluid in this case), which can be made once its final constitutive equations were derived. The equilibrium is defined so as to give the zero entropy production, cf. (3.220)–(3.222). To ensure the persistence of equilibrium (see the property S4 in Sect. 1.2), the regularity conditions (3.232)–(3.234) were added to the model of linear fluid. The majority of this section was devoted to the analysis of the stability of equilibrium; the concept of stable equilibrium was explained on page 127. The condition of stability called the Gibbs stability are (3.256) and (3.257). We

⁴⁸ Namely, we discuss two examples of equilibrium reversible processes: the isothermal and then those which are adiabatic. Such processes with ideal gas (i.e., with real stable gas at sufficiently low pressures) are used in the Carnot cycle in Appendix A.1.

The uniform process described here for linear fluid (see below (3.239) and (3.211)) which is *isothermal* (temperature $T = T^0$ is permanently the same constant) may be considered as a special case of equilibrium reversible processes in the fluid model B of Sect. 2.2 if the entropy production (given by (2.36) or (3.196)) may be neglected. A stable equilibrium state in a given instant has (besides the constant temperature T^0) the volume V (with zero velocity everywhere (3.223)). The change of this state to another one with the volume $V + dV$ (and the same temperature T^0 and zero velocity) by such a reversible process can be imagined as a sudden change of the volume by a small dV and as a development of this perturbed state isothermally to a new stable equilibrium state as described above (the second example without the body force: $\mathbf{b} = \mathbf{o}$ in (3.270)). A new equilibrium state will be practically achieved after a time interval much greater than the typical time scale in model B. Therefore the reversible process composed from sequences of such V to $V + dV$ changes must be slow \dot{V} is zero as well as the entropy production (2.36) and all this happens in the time scale of the model B. Heat exchange is nonzero and gives the entropy change, i.e., both members on the left-hand side of (3.274) compensate (similarly as in (2.10)) because the entropy production is zero (in (3.196) the second order contributions of heat and viscosity are neglected in fact, while in (3.274) the not neglected first order heat contribution is compensated).

want to stress that the latter condition enables the inversion of density as a function of pressure, i.e., it allows to use the pressure as an independent variable (in place of the density)—this condition was only supposed in preceding section and also in other thermodynamic approaches. During the evolution to the stable equilibrium state the entropy does not decrease in time, see (3.265) and also has an upper limit (3.264). Analogous conditions for the stability at different conditions (fluid of a constant volume maintained in a thermostat and under the effects of body forces) were derived in the form of canonical function defined by (3.277)—the conditions are given by (3.276) and (3.279).

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(Footnote 48 continued)

Quite analogously we can discuss the *adiabatic* reversible equilibrium process using the perturbation of the isolated body described above (the first example with persistent $\mathbf{i} = \mathbf{b} = \mathbf{o}$, $\mathbf{Q} = 0$, $\mathbf{q} = \mathbf{o}$). Starting with a corresponding equilibrium state in a given instant with the volume V (with zero velocity everywhere (3.223)) we obtain the new perturbed state changing suddenly the volume to $V + dV$ which develops as an isolated body into an equilibrium state with the new volume $V + dV$, isolated and with zero velocity everywhere. An adiabatic reversible process is obtained, continuing in this way sequentially (analogously as in the previous isothermal example). Such V to $V + dV$ changes must be again slow, with \dot{V} nearly zero as well as the entropy production (all members in (3.196) are neglected, i.e., equality in (2.36) is valid in the time scale of model B). But then the left-hand side of (3.265) is nearly zero and entropy remains constant during such a reversible adiabatic process.

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