IRREVERSIBLE (RATIONAL) THERMODYNAMICS OF FLUID-SOLID MIXTURES

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Reversible and irreversible (transport) phenomena in fluid-solid mixtures were analysed by the method of rational thermodynamics (nonlinear continuum mechanics). After formulating the balances and the second law of thermodynamics, constitutive equations for the binary mixture were proposed involving diffusion, heat conduction, and long-term memory characterized by an internal parameter. Viscosity and chemical reactions were disregarded. The final form of the constitutive equations is based on the constitutive principles of determinism, local action, memory, equipresence, objectivity, and on the entropic principle of Coleman and Noll. The cases of an isotropic solid and a mixture of fluids are also discussed.

The present work deals with a phenomenological (*i.e.* not molecular) description of reversible and irreversible (*e.g.* transport) phenomena in mixtures of a fluid and a substance of any symmetry (usually solid) using the method of nonlinear continuum mechanics, called also rational thermodynamics[1-4]. The results are intended for the phenomenological description of gas diffusion in polymers[5,6], since certain phenomena (*e.g.* nonfickian diffusion) are difficult to describe in terms of older theories. Although the results are valid for the nonlinear case, they can be simplified (*e.g.* by linearization) and used in further work[5]. The procedure will be similar to the monograph[2], where the underlying ideas, principles, and postulates are discussed (compare[1,3,4]): rational thermodynamics (nonlinear thermomechanics) will be applied to a nonreacting two-component mixture of a fluid and a substance of arbitrary symmetry (*e.g.* as a model of gas penetrating through a polymer[5,6], usually a solid, which may have anisotropic properties). The viscosity effects will be neglected as well as chemical reactions between gas and polymer. On the other hand, a long-term memory describing physical or chemical changes in the polymer will be taken into account by using internal ("hidden") parameters.

Basic Concepts and Kinematics

We shall use the direct notation of vectors and tensors (denoted respectively by small and capital bold face letters) with the usual notation of the common operations[1-4] in addition to the notation of the components in cartesian coordinates using the summation rule. The components will be distinguished by latin superscripts: capital in the case of reference (Lagrangian) and small in the case of spatial (Euler) coordinates necessary for the description of deformations[1-4]. The spatial and reference gradients of a quantity ψ will be denoted respectively as grad ψ and Grad ψ. For example, when $\boldsymbol{F}$ (in component form F^{iJ}) is the deformation gradient[1-4], then the second deformation gradient is $\mathbf{G} \equiv \text{Grad}\, \boldsymbol{F}$ (in component form G^{iJK}; the last superscript refers to the component of the gradient). Or, for vector $\boldsymbol{a}$

$$\text{grad}\, \boldsymbol{a} = (\text{Grad}\, \boldsymbol{a})\, \boldsymbol{F}^{-1}\,,$$
$$(\text{grad}\, \boldsymbol{a})^{ij} = (\text{Grad}\, \boldsymbol{a})^{iJ}\, F^{-1Jj}\,, \tag{1}$$

where $\boldsymbol{F}^{-1}$ is inverse to $\boldsymbol{F}$.

The mixture components are referred to by subscripts α = g, s, of which g refers to the fluid (liquid or gas) and s to a substance of arbitrary symmetry (preferably solid polymer); the summation over both components will be denoted as $\sum$. In some cases the subscripts may be omitted without loss in clarity, *e.g.* the deformation gradients refer only to the solid, the subscript s being superfluous.

We introduce the diffusion velocity $\boldsymbol{u}$ defined as

$$\boldsymbol{u} = \boldsymbol{v}_g - \boldsymbol{v}_s\,, \tag{2}$$

i.e. the difference between the component velocities $\boldsymbol{v}_g$ and $\boldsymbol{v}_s$. The material derivative with respect to component α, *e.g.* for tensor $\boldsymbol{A}$ is defined as

$$\frac{\mathrm{D}_\alpha \boldsymbol{A}}{\mathrm{D}t} = \frac{\partial \boldsymbol{A}}{\partial t} + (\text{grad}\, \boldsymbol{A})\, \boldsymbol{v}_\alpha\,, \tag{3}$$

where the derivative with respect to time t is taken at constant position in the space coordinates. We can write shortly

$$\dot{\boldsymbol{A}} \equiv \frac{\mathrm{D}_s \boldsymbol{A}}{\mathrm{D}t} \tag{4}$$

and in the component form

$$\frac{\mathrm{D}_g A^{JK}}{\mathrm{D}t} = \dot{A}^{JK} + u^i (\text{grad}\, \boldsymbol{A})^{JKi}\,. \tag{5}$$

The spatial velocity gradient $\boldsymbol{L}_\alpha$ is according to Eq. (*1*)

$$\boldsymbol{L}_\alpha \equiv \text{grad}\, \boldsymbol{v}_\alpha = \frac{\mathrm{D}_\alpha \boldsymbol{F}_\alpha}{\mathrm{D}t}\, \boldsymbol{F}_\alpha^{-1} \tag{6}$$

and can be decomposed into a symmetrical tensor of the deformation rate, $\boldsymbol{D}_\alpha$, and an antisymmetrical tensor spin, $\boldsymbol{W}_\alpha$

$$\boldsymbol{L}_\alpha = \boldsymbol{D}_\alpha + \boldsymbol{W}_\alpha . \tag{7}$$

General Postulates

We shall consider the conservation laws and the second law of thermodynamics in a local form for chemically nonreacting mixtures (ref.[2], part III). The mass balance for component α reads

$$\frac{D_\alpha \varrho_\alpha}{Dt} + \varrho_\alpha \operatorname{div} \boldsymbol{v}_\alpha = 0 , \tag{8}$$

where ϱ_α is the density of component α ("weight concentration") which is always positive. Eq. (*8*) can be integrated to give for the solid (ref.[2], Eq. (*27.12*))

$$\varrho_s |\det \boldsymbol{F}| = \varrho_s^0 , \tag{9}$$

where ϱ_s^0 is the prescribed density of component s in reference configuration. The summation of Eq. (*8*) over both components gives the mass balance of the mixture.

The momentum balance for component α reads

$$\varrho_\alpha \frac{D_\alpha \boldsymbol{v}_\alpha}{Dt} = \operatorname{div} \boldsymbol{T}_\alpha + \varrho_\alpha \boldsymbol{b}_\alpha + \boldsymbol{k}_\alpha , \tag{10}$$

where $\boldsymbol{T}_\alpha$ denotes partial stress tensor, $\boldsymbol{b}_\alpha$ external volume force, *e.g.* gravity (if the reference system is not inertial, then the corresponding force, *e.g.* centrifugal, is involved), and $\boldsymbol{k}_\alpha$ denotes interaction volume force (acting on component α from the other). The momentum balance for the mixture reads

$$\sum \boldsymbol{k}_\alpha = \boldsymbol{o} . \tag{11}$$

Hence, only $\boldsymbol{k} \equiv \boldsymbol{k}_s$ will be used in the text below. The balance of the moment of momentum for component α (assumed to be mechanically nonpolar) has the form

$$\boldsymbol{T}_\alpha = \boldsymbol{T}_\alpha^T , \tag{12}$$

where the superscript T denotes transposition. The corresponding equation for the mixture is obtained again by summation.

Since both components have the same temperature, we need the energy balance only for the mixture (ref.[2], section 31):

$$\sum \varrho_\alpha \frac{D_\alpha u_\alpha}{Dt} = \sum \mathrm{tr}\, \mathbf{T}_\alpha \mathbf{D}_\alpha - \mathrm{div}\, \mathbf{q} + Q - \mathbf{k} \,.\, \mathbf{u} \,. \qquad (13)$$

Here, u_α is the (specific) internal energy of component α, $\mathbf{q}$ the heat flux, Q the heat source (due to external radiation), tr denotes trace, and div divergence in spatial coordinates.

The second law of thermodynamics can be written in the form of the Clausius–-Duhem inequality[2–4]

$$\sigma \equiv \sum \varrho_\alpha \frac{D_\alpha s_\alpha}{Dt} + \mathrm{div}\, \mathbf{q}/T - Q/T \geqq 0 \,, \qquad (14)$$

where s_α is the (specific) entropy of component α, T is the absolute temperature, which is positive, and σ entropy production. By combining Eqs (13) and (14) we obtain the so-called reduced inequality

$$-T\sigma = \sum \varrho_\alpha \frac{D_\alpha f_\alpha}{Dt} + \sum \varrho_\alpha s_\alpha \frac{D_\alpha T}{Dt} + T^{-1} \mathbf{q} \,.\, \mathbf{g} - \sum \mathrm{tr}\, \mathbf{T}_\alpha \mathbf{D}_\alpha + \mathbf{k} \,.\, \mathbf{u} \leqq 0 \,, \qquad (15)$$

where $\mathbf{g} \equiv \mathrm{grad}\, T$ and the specific free energy, f_α, of component α is defined as

$$f_\alpha \equiv u_\alpha - T s_\alpha \,. \qquad (16)$$

Constitutive Equations

The general postulates are insufficient for the solution of a given problem; they must be supplemented with equations describing the studied material model, *i.e.* constitutive equations. These are based on the so-called constitutive principles[1–4]. According to the principle of determinism, the independent variables of the constitutive equations are determined by the field of motion of the components and by the temperature field; according to the principles of local action and differential memory the constitutive equations represent functions in the space and time derivatives of these fields; and according to the principle of equipresence all dependent variables are functions of the same independent variables. For a nonreacting two-component mixture with constant temperature, we propose the constitutive equations for the dependent variables (which follow from the general postulates) in the form

$$\{f_\alpha, s_\alpha, \mathbf{T}_\alpha(\mathrm{sym.}), \mathbf{k}, \mathbf{q}, \beta\} = \mathscr{F}(\varrho_g, \mathbf{F}, \mathbf{h}, \mathbf{G}, \mathbf{u}, T, \mathbf{g}, \beta) \qquad (17)$$

which summarizes nine constitutive equations for the quantities on the left-hand side, *i.e.* $\mathscr{F}$ represents in turn the functions $\hat{f}_\alpha$, $\hat{s}_\alpha$, $\hat{\mathbf{T}}_\alpha$, $\hat{\mathbf{k}}$, $\hat{\mathbf{q}}$, and $\hat{l}$ (see Eq. (*18*) below) of the independent variables on the right-hand side. Of these, $\boldsymbol{F}$, $\mathbf{G}$, ϱ_g and $\boldsymbol{h} \equiv \operatorname{grad} \varrho_g$ characterize deformations; for the fluid, the deformation can be expressed by the density[1-3,9]. The quantities $\mathbf{G}$ and $\boldsymbol{h}$ have to be used with mixtures to describe interactions between the components (the simpler case, so-called mixtures of simple materials, will be discussed in the next section)[2-4]. A short-term memory related to motion is given by the dependence on the velocities $\mathbf{v}_\alpha$ through the diffusion rate $\boldsymbol{u}$ (as a result of the principle of objectivity, discussed below); the effect of viscosity is ignored (the quantities in Eq. (*7*) are absent in Eq. (*17*)). The temperature field has an effect only through the temperature T and its gradient $\mathbf{g}$, the temperature memory being ignored. The long-term memory is characterized by the scalar internal parameter β by using the constitutive equation for its time derivative[7]

$$\dot{\beta} = \hat{l}(\varrho_g, \boldsymbol{F}, \boldsymbol{h}, \mathbf{G}, \boldsymbol{u}, T, \mathbf{g}, \beta)\,. \qquad (18)$$

For simplicity, only one internal parameter is considered, however the following equations may easily be generalized for more such parameters.

The constitutive equations (*17*) involve implicitly the constitutive objectivity principle[1-4], *i.e.* independence of the constitutive equations or the material model on the reference frame, since the velocities of the components are involved only in the relative velocity $\boldsymbol{u}$. In addition, the principle of objectivity implies that the constitutive functions $\mathscr{F}$ are isotropic, *i.e.*

$$\{f_\alpha, s_\alpha, \mathbf{Q}\boldsymbol{T}_\alpha \mathbf{Q}^{\mathrm{T}}, \mathbf{Q}\boldsymbol{k}, \mathbf{Q}\boldsymbol{q}, \dot{\beta}\} = \mathscr{F}(\varrho_g, \mathbf{Q}\boldsymbol{F}, \mathbf{Q}\boldsymbol{h}, \mathbf{Q}\mathbf{G}, \mathbf{Q}\boldsymbol{u}, T, \mathbf{Q}\mathbf{g}, \beta) \qquad (19)$$

for all orthogonal tensors $\mathbf{Q}$, *i.e.* for arbitrary rotation and inversion.

In order to use the most important constitutive principle, the entropy principle of Coleman and Noll[8], we apply the derivative (*4*) to the constitutive functions $\hat{f}_\alpha$:

$$\begin{aligned}\dot{f}_\alpha = {} & \frac{\partial \hat{f}_\alpha}{\partial F^{iJ}} (W_s^{ij} F^{jJ} + D_s^{ij} F^{jJ}) - \frac{\partial \hat{f}_\alpha}{\partial \varrho_g} (\varrho_g D_g^{ii} + u^i h^i) + \frac{\partial \hat{f}_\alpha}{\partial T} \dot{T} + \frac{\partial \hat{f}_\alpha}{\partial g^j} \dot{g}^j + \frac{\partial \hat{f}_\alpha}{\partial \beta} \dot{\beta} + \\ & + \frac{\partial \hat{f}_\alpha}{\partial u^j} \dot{u}^j + \frac{\partial \hat{f}_\alpha}{\partial G^{jJK}} \dot{G}^{jJK} - \frac{\partial \hat{f}_\alpha}{\partial h^i} [u^j (\operatorname{grad} \boldsymbol{h})^{ij} + (h^j \delta^{ki} + h^i \delta^{jk}) D_g^{jk} - h^j W_g^{ji} - \\ & - \varrho_g (\operatorname{grad} \operatorname{tr} \mathbf{D})^i]\,. \end{aligned} \qquad (20)$$

Here, use was made of Eqs (*5*)–(*8*) (δ^{ik} denotes Kronecker's delta). This result is substituted for $D_\alpha f_\alpha/Dt$ into the reduced inequality (*15*), where $D_g f_g/Dt$ is expressed by using Eq. (*5*) and grad f_g by means of the constitutive function $\hat{f}_g$ (as Eq. (*20*)) and Eq. (*1*). Similarly in Eq. (*15*) $D_g T/Dt$ is modified by using Eq. (*5*). Further we use the definitions of the density of the mixture ϱ, its free energy f, and entropy s

$$\varrho \equiv \sum \varrho_\alpha\,, \quad \varrho f \equiv \sum \varrho_\alpha f_\alpha\,, \tag{21),(22}$$

$$\varrho s \equiv \sum \varrho_\alpha s_\alpha\,, \tag{23}$$

where f and s are functions $\hat{f}$ and $\hat{s}$ of the independent variables in Eq. (*17*), since ϱ_s according to Eq. (*9*) depends on $\mathbf{F}$. Finally, we obtain the inequality

$$\begin{aligned}
-T\sigma = {} & \varrho\left(\frac{\partial \hat{f}}{\partial T} + s\right)\dot{T} + \varrho\frac{\partial \hat{f}}{\partial u^j}\dot{u}^j + \varrho\frac{\partial \hat{f}}{\partial g^j}\dot{g}^j - \varrho\frac{\partial \hat{f}}{\partial h^j}\varrho_g(\operatorname{grad}\operatorname{tr}\mathbf{D})^j + \\
& + \varrho\frac{\partial \hat{f}}{\partial G^{jJK}}\dot{G}^{jJK} + \varrho_g\frac{\partial \hat{f}_g}{\partial g^j}u^i(\operatorname{grad}\mathbf{g})^{ji} + \left(\varrho_g\frac{\partial \hat{f}_g}{\partial h^j}u^i - \varrho\frac{\partial \hat{f}}{\partial h^i}u^j\right)(\operatorname{grad}\mathbf{h})^{ji} + \\
& + \varrho_g\frac{\partial \hat{f}_g}{\partial G^{jJK}}F^{-1Li}u^i(\operatorname{Grad}\mathbf{G})^{jJKL} + \varrho_g\frac{\partial \hat{f}_g}{\partial \beta}u^i(\operatorname{grad}\beta)^i - \\
& - \left[T_g^{ij} + \delta^{ij}\sum \varrho_\alpha\varrho_g\frac{\partial \hat{f}_\alpha}{\partial \varrho_g} - \varrho_g\frac{\partial \hat{f}_g}{\partial u^i}u^j + \varrho\frac{\partial \hat{f}}{\partial h^k}(h^j\delta^{ik} + h^k\delta^{ji})\right]D_g^{ij} - \\
& - \left[T_s^{ij} - \sum \varrho_\alpha\frac{\partial \hat{f}_\alpha}{\partial F^{iJ}}F^{jJ} + \varrho_g\frac{\partial \hat{f}_g}{\partial u^i}u^j\right]D_s^{ij} + \left[\varrho_g\frac{\partial \hat{f}_g}{\partial u^i}u^j + \varrho\frac{\partial \hat{f}}{\partial h^i}h^j\right]W_g^{ij} - \\
& - \left[\varrho_g\frac{\partial \hat{f}_g}{\partial u^i}u^j - \sum \varrho_\alpha\frac{\partial \hat{f}_\alpha}{\partial F^{iJ}}F^{jJ}\right]W_s^{ij} - \varrho_s\frac{\partial \hat{f}_s}{\partial \varrho_g}u^i h^i + \varrho_g\frac{\partial \hat{f}_g}{\partial F^{jJ}}F^{-1Ki}G^{jJK}u^i + \\
& + \varrho_g\left(\frac{\partial \hat{f}_g}{\partial T} + s_g\right)u^i g^i + T^{-1}q^i g^i + k^i u^i + \varrho\frac{\partial \hat{f}}{\partial \beta}\dot{\beta} \leqq 0\,.
\end{aligned} \tag{24}$$

We now apply the constitutive entropic principle to this inequality[1–4,8]: the second law (*14*) and hence also inequality (*24*) must be valid for any motion and temperature fields in the material, hence for any values of the independent variables ϱ_g, $\mathbf{F}$, $\mathbf{h}$, $\mathbf{G}$, $\mathbf{u}$, T, $\mathbf{g}$, and parameter β obtained by solving Eq. (*18*) (we assume the existence of the solution at any initial values of this parameter[7]) and further for arbitrary values of the mutually independent quantities

$$\dot{T},\ \dot{\mathbf{u}},\ \dot{\mathbf{g}},\ \operatorname{grad}\operatorname{tr}\mathbf{D} \tag{25}$$

$$\mathbf{W}_g,\ \mathbf{W}_s \tag{26}$$

$$\operatorname{grad}\mathbf{g},\ \operatorname{grad}\mathbf{h},\ \mathbf{D}_g,\ \mathbf{D}_s \tag{27}$$

$$\dot{\mathbf{G}},\ \operatorname{Grad}\mathbf{G} \tag{28}$$

$$\operatorname{grad}\beta\,. \tag{29}$$

These quantities are involved in the expression (*24*) in the linear form, which however must be cancelled (in the opposite case it would be possible to find such values of (*25*)–(*29*) which would make the inequality (*24*) invalid). To cancel the terms involving the quantities (*25*), we must set

$$\frac{\partial \hat{f}}{\partial \boldsymbol{u}} \equiv \mathbf{o}\,, \quad \frac{\partial \hat{f}}{\partial \boldsymbol{g}} \equiv \mathbf{o}\,, \quad \frac{\partial \hat{f}}{\partial \boldsymbol{h}} \equiv \mathbf{o}\,, \tag{30}$$

$$\frac{\partial \hat{f}}{\partial T} = -s\,. \tag{31}$$

This leads to simplification. Further, since the terms (*26*) are antisymmetrical, their multipliers in the expression (*25*) must be symmetrical

$$\frac{\partial \hat{f}_\alpha}{\partial u^i} u^j = \frac{\partial \hat{f}_\alpha}{\partial u^j} u^i \qquad \alpha = \mathrm{g, s} \tag{32}$$

(for $\alpha = \mathrm{s}$, use was made of the first of Eqs (*30*)) and also

$$\sum \varrho_\alpha \frac{\partial \hat{f}_\alpha}{\partial F^{ij}} F^{jj} = \sum \varrho_\alpha \frac{\partial \hat{f}_\alpha}{\partial F^{jj}} F^{ij}\,. \tag{33}$$

For analogous reason, to cancel the quantities containing (*27*), we must set

$$\varrho_\mathrm{g} \frac{\partial \hat{f}_\mathrm{g}}{\partial g^j} u^i + \varrho_\mathrm{g} \frac{\partial \hat{f}_\mathrm{g}}{\partial g^i} u^j = 0\,. \tag{34}$$

Here, the derivatives, which generally are functions of $\boldsymbol{u}$ continuous at the point $\boldsymbol{u} = \mathbf{o}$, must be identically equal to zero (this can be shown by setting $\mathrm{i} = \mathrm{j}$). Thus, the first two terms of (*27*) give

$$\frac{\partial \hat{f}_\mathrm{g}}{\partial \boldsymbol{g}} \equiv \mathbf{o}\,, \quad \frac{\partial \hat{f}_\mathrm{g}}{\partial \boldsymbol{h}} \equiv \mathbf{o}\,. \tag{35}$$

Similar considerations for the last two terms of (*27*) using Eqs (*30*) (third one), (*32*), (*33*), and (*12*) give

$$T_\mathrm{g}^{ij} = -\sum \varrho_\alpha \varrho_\mathrm{g} \frac{\partial \hat{f}_\alpha}{\partial \varrho_\mathrm{g}} \delta^{ij} + \varrho_\mathrm{g} \frac{\partial \hat{f}_\mathrm{g}}{\partial u^i} u^j\,, \tag{36}$$

$$T_\mathrm{s}^{ij} = \sum \varrho_\alpha \frac{\partial \hat{f}_\alpha}{\partial F^{ij}} F^{jj} - \varrho_\mathrm{g} \frac{\partial \hat{f}_\mathrm{g}}{\partial u^i} u^j\,. \tag{37}$$

The first of the terms (*28*) is a tensor of the third order, symmetrical in the last two indices, hence its multiplier in (*24*) must be a similar antisymmetrical tensor. This is, however, symmetrical in these indices (derivatives with respect to symmetrical quantities preserve the symmetry, ref.[2], appendix C), hence identically

$$\frac{\partial \hat{f}}{\partial G^{iJK}} \equiv 0 \,. \tag{38}$$

The second one of the terms (*28*) is a tensor of the fourth order, symmetrical in the last three indices (ref.[2], (A 67)). A tensor of the third order, symmetrical in the last two indices and defined as (for $\boldsymbol{u} \neq \mathbf{o}$)

$$A^{jJK} \equiv F^{-1Li} u^i (\mathrm{Grad}\ \mathbf{G})^{jJKL} \,, \tag{39}$$

may be arbitrary since Grad $\mathbf{G}$ is arbitrary and the vector $F^{-1Li}u^i$ is different from zero (det $\mathbf{F} \neq 0$). Further procedure is the same as in deriving Eq. (*38*), only Eq. (*39*) is substituted for $\dot{\mathbf{G}}$. Hence,

$$\frac{\partial \hat{f}_g}{\partial G^{iJK}} \equiv 0 \,. \tag{40}$$

Here, the validity of Eq. (*39*) is generalized for the case $\boldsymbol{u} = \mathbf{o}$ assuming continuity of the derivative at this point.

At last, the multiplier of the term (*29*) in the expression (*24*) must also be equal to zero. This can be chosen independently of the value of β, since the initial value for the solution of the differential equations (*18*) can be chosen independently for different particles and the zero of the time scale is arbitrary. For the inequality (*24*) to hold good with any values of grad β, we must set

$$\frac{\partial \hat{f}_g}{\partial \beta} \equiv 0 \tag{41}$$

including the point $\boldsymbol{u} = \mathbf{o}$, where the derivative is again assumed to be continuous.

According to Eqs (*30*) and (*38*)

$$f = \hat{f}(\varrho_g, \mathbf{F}, T, \beta) \,. \tag{42}$$

The entropy s depends on the same variables, as can be seen from Eq. (*31*). According to Eqs (*35*), (*40*), and (*41*) we have

$$f_g = \hat{f}_g(\varrho_g, \mathbf{F}, \boldsymbol{u}, T) \,, \tag{43}$$

$$f_s = \hat{f}_s(\varrho_g, \mathbf{F}, \boldsymbol{u}, T, \beta) \,. \tag{44}$$

The last equation follows from Eqs (*42*), (*43*), and (*22*) (see text below Eq. (*22*)). Such simplification does not, in general, apply for the partial entropy s_α, and we must observe Eq. (*17*) instead.

The inequality (*24*) is, after all, reduced to

$$\Pi \equiv -T\sigma = k^i u^i - \varrho_s \frac{\partial \hat{f}_s}{\partial \varrho_g} h^i u^i + \varrho_g \frac{\partial \hat{f}_g}{\partial F^{jJ}} F^{-1Ki} G^{jJK} u^i + + \varrho_g \left(\frac{\partial \hat{f}_g}{\partial T} + s_g \right) u^i g^i + T^{-1} q^i g^i + \varrho \frac{\partial \hat{f}}{\partial \beta} \dot{\beta} \leqq 0 \,, \qquad (45)$$

where $\Pi = \hat{\Pi}(\varrho_g, \mathbf{F}, \mathbf{h}, \mathbf{G}, \mathbf{u}, T, \mathbf{g}, \beta)$.

It can be seen from the constitutive equations for our model that the specific free energies are given by Eqs (*42*)–(*44*); the specific entropy s is given analogously (through Eq. (*31*)). The stress tensors $\mathbf{T}_\alpha$ are given by Eqs (*36*) and (*37*); generally, $\mathbf{T}_g$ is in the case of diffusion ($\mathbf{u} \neq \mathbf{o}$) not reduced to the pressure. Other constitutive equations remain in the form (*17*) (including s_α); the entropy production is given by Eq. (*45*). Up to this point, we did not use the constitutive principle of symmetry (ref.[2], section 19) related to the eventual symmetry of the material (*e.g.* isotropy), which will be discussed in the last section.

Considering zero production of entropy, we define the equilibrium by the conditions

$$\mathbf{u} = \mathbf{o} \,, \quad \mathbf{g} = \mathbf{o} \qquad (46)$$

and by the value of the internal parameter

$$\beta = \beta^+ \qquad (47)$$

at which $\dot{\beta}$ is equal to zero

$$\dot{\beta} = \hat{l}(\varrho_g, \mathbf{F}, \mathbf{h}, \mathbf{G}, \mathbf{o}, T, \mathbf{o}, \beta^+) = 0 \,. \qquad (48)$$

Then, the quantity Π defined by Eq. (*45*) is not only zero but also minimum, *i.e.*

$$\frac{\mathrm{d}\Pi}{\mathrm{d}\lambda} (\varrho_g, \mathbf{F}, \mathbf{h}, \mathbf{G}, \lambda\mathbf{u}, T, \lambda\mathbf{g}, \beta^+ + \lambda\nu) = 0 \qquad (49)$$

for the real parameter λ equal to zero (ν is a constant scalar).

This in turn implies that in the equilibrium state we have

$$\mathbf{q}^+ = \mathbf{o} \,, \qquad (50)$$

$$k^{+i} = \varrho_s \left(\frac{\partial \hat{f}_s}{\partial \varrho_g}\right)^+ h^i - \varrho_g \left(\frac{\partial \hat{f}_g}{\partial F^{iJ}}\right)^+ F^{-1Ki} G^{iJK}, \tag{51}$$

$$\left(\frac{\partial \hat{f}}{\partial \beta}\right)^+ = 0. \tag{52}$$

Here, the cross refers to equilibrium values, *i.e.* values obtained by introducing the conditions (*46*) and (*47*) into the corresponding constitutive equations, *e.g.* $\mathbf{q}^+ = \hat{\mathbf{q}}(\varrho_g, \mathbf{F}, \mathbf{h}, \mathbf{G}, \mathbf{o}, T, \mathbf{o}, \beta^+)$ or $(\partial \hat{f}/\partial \beta)^+ = (\partial \hat{f}/\partial \beta)\,(\varrho_g, \mathbf{F}, T, \beta^+)$. Eqs (*50*)–(*52*) follow by substituting Eq. (*45*) into (*49*), observing the arbitrariness in the values of $\mathbf{u}$, $\mathbf{g}$, and v, and assuming $(\partial \hat{l}/\partial \beta)^+ \neq 0$.

Thus, in the equilibrium (*46*) and (*47*) the heat flux (*50*) and the "affinity" (*52*) are equal to zero and $\mathbf{k}$ is given by Eq. (*51*). Another restriction of the constitutive equations follows from the second derivatives of Π (conditions for the minimum, expressed by inequalities).

Simplified Material Models

By omitting some independent variables in the constitutive equations, simplified material models can be obtained. It is not sufficient, however, only to reduce the resulting equations in the preceding section. Further reduction is carried out by applying anew the entropic principle to the inequality (*45*). For example, with a mixture of simple materials, the independent variables $\mathbf{h}$ and $\mathbf{G}$ are omitted from the constitutive equations (*17*). The relation (*45*) is then linear in these quantities and the entropy principle leads to

$$\frac{\partial \hat{f}_s}{\partial \varrho_g} \equiv 0, \quad \frac{\partial \hat{f}_g}{\partial \mathbf{F}} \equiv \mathbf{O} \tag{53}$$

(we assume continuity of the derivatives at $\mathbf{u} = \mathbf{o}$ as in the derivation of Eq. (*35*)). The free energies of the components hence depend only on their own density and deformation gradient, which is a characteristic property of all simple materials[2–4]. In the equilibrium state defined by Eqs (*46*)–(*48*) we have $\mathbf{k}^+ = \mathbf{o}$ in addition to the conditions (*50*) and (*52*). Such a mixture consists of components the interactions of which are negligible.

We now shall consider a mixture of nonsimple materials without internal parameters, *i.e.* without a long-term memory: the parameter β is cancelled from the constitutive equations (*17*), (*42*), and (*44*) as well as the last term in the relation (*45*). The internal parameters of the material decrease rapidly with the time, the values of $\beta = \beta^+$ and $\dot{\beta} = 0$ being constant.

The next section deals with a simplification of the general model.

Linear Model

The general equations can be simplified by assuming that

1) the constitutive equations are linear with respect to

$$\boldsymbol{u}, \boldsymbol{g}, \boldsymbol{h}, \mathbf{G} \tag{54}$$

2) the constitutive equation for $\dot{\beta}$ (*18*) is independent of the quantities (*54*) and has the form

$$\dot{\beta} = \hat{l}(\varrho_g, \mathbf{F}, T, \beta)\,. \tag{55}$$

We start with the assumption that the constitutive equations (*17*), (*42*)–(*44*) are linear with respect to the diffusion velocity $\boldsymbol{u}$. This is of advantage in studying the diffusion, since both $\boldsymbol{u}$ and the diffusion flux can be expressed explicitly from the constitutive equations. However, if the specific free energies (*43*) and (*44*) are forced to be linear functions of $\boldsymbol{u}$, they cannot depend on $\boldsymbol{u}$ at all, as can be seen from Eq. (*32*), hence

$$f_g = \hat{f}_g(\varrho_g, \mathbf{F}, T)\,, \quad f_s = \hat{f}_s(\varrho_g, \mathbf{F}, T, \beta)\,. \qquad (56), (57)$$

Equations (*36*) and (*37*) are then reduced to

$$\boldsymbol{T}_g = -P_g \mathbf{1}\,, \quad P_g \equiv \sum \varrho_\alpha \varrho_g \frac{\partial \hat{f}_\alpha}{\partial \varrho_g}\,, \qquad (58), (59)$$

i.e. the tensor $\boldsymbol{T}_g$ is reduced to partial pressure, $P_g = \hat{P}_g(\varrho_g, \mathbf{F}, T, \beta)$ and

$$T_s^{ij} = \sum \varrho_\alpha \frac{\partial \hat{f}_\alpha}{\partial F^{iJ}} F^{jJ}\,. \tag{60}$$

The quantity f satisfies Eq. (*42*) (analogously for s according to Eq. (*31*)). If we consider the linearity with respect to all the variables (*54*), other constitutive equations will have the quite general form

$$s_\alpha = s_{0\alpha} + s^i_{1\alpha} u^i + s^i_{2\alpha} g^i + s^i_{3\alpha} h^i + S^{iJK}_{4\alpha} G^{iJK}\,, \tag{61}$$

where the coefficients $s_{0\alpha}$, $s^i_{r\alpha}$ $(r = 1, 2, 3)$, and $S^{iJK}_{4\alpha}$ are functions of ϱ_g, $\mathbf{F}$, T, and β. Because of the symmetry of the term G^{iJK}, the term $S^{iJK}_{4\alpha}$ is symmetrical in the indices J and K. The constitutive equation for u_α, according to Eqs (*16*), (*56*), (*57*), and (*61*), would have a similar form; and the same applies to the constitutive equation for the general case (*18*) (since the equations for such a general, even if linearized case are very complicated, use was made of the simplifying assumption (*55*)). Finally, constitutive equations for the vectors $\boldsymbol{k}$ and $\boldsymbol{q}$ linearized with respect to the quantities (*54*) will have the quite general form

$$k^{i} = k_{0}^{i} - K_{1}^{ij}u^{j} - K_{2}^{ij}g^{j} + K_{3}^{ij}h^{j} + K_{4}^{ijJK}G^{jJK}\,, \tag{62}$$

$$q^{i} = q_{0}^{i} - Q_{1}^{ij}u^{j} - Q_{2}^{ij}g^{j} + Q_{3}^{ij}h^{j} + Q_{4}^{ijJK}G^{jJK}\,, \tag{63}$$

where all the coefficients k_0^i, K_r^{ij}, K_4^{ijJK}, q_0^i, Q_r^{ij}, and Q_4^{ijJK} ($r = 1, 2, 3$) are functions of ϱ_g, $\boldsymbol{F}$, T, and β, and the coefficients K_4^{ijJK}, Q_4^{ijJK} are symmetrical in J, K (because of the same symmetry of G^{jJK}). The negative signs in Eqs (*62*) and (*63*) were chosen in order to obtain positive values of the most common transport coefficients (ref.[5]; compare discussion of the equilibrium in the next section).

Constitutive Equations for the Linear Model

As with every simplified model, further restrictions can be obtained by applying once more the entropic principle to the inequality (*45*), into which the simplified constitutive equations (*56*), (*57*), (*61*)–(*63*) were introduced. Thus,

$$\begin{aligned}
-T\sigma = {} & \varrho \frac{\partial \hat{f}}{\partial \beta}\,\dot{\beta} + k_0^i u^i + T^{-1} q_0^i g^i + \left(K_3^{ij} - \varrho_s \frac{\partial \hat{f}_s}{\partial \varrho_g}\,\delta^{ij}\right) h^j u^i + \\
& + T^{-1} Q_3^{ij} h^j g^i + \left[\varrho_g \left(\frac{\partial f_g}{\partial T} + s_{0g}\right)\delta^{ij} - K_2^{ji} - T^{-1} Q_1^{ij}\right] g^i u^j + \\
& + \left(K_4^{ijJK} + \varrho_g \frac{\partial \hat{f}_g}{\partial F^{iJ}}\,F^{-1Ki}\right) G^{jJK} u^i + T^{-1} Q_4^{ijJK} G^{jJK} g^i - K_1^{ij} u^i u^j - \\
& - T^{-1} Q_2^{ij} g^j g^i + \varrho_g s_{3g}^j h^j u^i g^i + \varrho_g S_{4g}^{jJK} G^{jJK} u^i g^i + \\
& + \varrho_g s_{1g}^j u^j u^i g^i + \varrho_g s_{2g}^j g^j g^i u^i \leqq 0\,.
\end{aligned} \tag{64}$$

Now, we use again the entropic principle of Coleman and Noll[1–4,8]: The first term and other coefficients combined with the quantities (*54*) are functions only of ϱ_g, $\boldsymbol{F}$, T, and β; if these variables are chosen constant, the quantities (*54*) become constants, although arbitrary. Thus, considering the terms of the second order linear with respect to $\boldsymbol{h}$ and $\mathbf{G}$ we obtain the identitities

$$Q_3^{ij} \equiv 0\,, \quad K_3^{ij} = \varrho_s \frac{\partial \hat{f}_s}{\partial \varrho_g}\,\delta^{ij}\,, \tag{65), (66}$$

$$Q_4^{ijJK} \equiv 0\,, \quad K_4^{ijJK} = -\frac{1}{2}\varrho_g\left(\frac{\partial \hat{f}_g}{\partial F^{jJ}}F^{-1Ki} + \frac{\partial \hat{f}_g}{\partial F^{jK}}F^{-1Ji}\right). \qquad (67), (68)$$

The last two equations follow from the antisymmetry of the coefficients standing before $G^{jJK}g^i$ and $G^{jJK}u^i$ (since $\mathbf{G}$ is symmetrical in J, K) and from the symmetry of Q_4^{ijJK} and K_4^{ijJK}. We assumed $\boldsymbol{g} = \mathbf{o}$ in the derivation of Eqs (66) and (68), and $\boldsymbol{u} = \mathbf{o}$ in the derivation of (65) and (67) to eliminate the terms of the third order, which are also linear with respect to $\boldsymbol{h}$ and $\mathbf{G}$. This linearity can be used together with Eqs (65)–(68) to show that

$$s_{3g}^j \equiv 0\,, \quad S_{4g}^{jJK} \equiv 0\,. \qquad (69)$$

(Note that $S_{4\alpha}^{jJK}$ is symmetrical in J and K). With the remaining terms of the third order, it is important that for sufficiently large values of the components of $\boldsymbol{u}$ and $\boldsymbol{g}$ these terms determine the sign of the inequality (64). For example, if we set $\boldsymbol{u} = \boldsymbol{g} = (a, 0, 0)$, where a is an arbitrarily large (positive or negative) number, then $s_{1g}^1 + s_{2g}^1 = 0$. If we set $\boldsymbol{u} = (a, 0, 0)$, $\boldsymbol{g} = (a, a, 0)$, we obtain $s_{1g}^1 + s_{2g}^1 + s_{2g}^2 = 0$, and therefore (proceeding analogously in remaining cases)

$$s_{1g}^i \equiv 0\,, \quad s_{2g}^i \equiv 0\,. \qquad (70)$$

It follows from Eqs (31), (42), (23), and (9) that the identities (69) and (70) apply not only to the component g but also to the other, s. Hence,

$$s_\alpha = \hat{s}_\alpha(\varrho_g, \mathbf{F}, T, \beta) \qquad \alpha = \mathrm{s}, \mathrm{g}\,. \qquad (71)$$

The constitutive equations (62) and (63) then take the form

$$k^i = k_0^i - K_1^{ij}u^j - K_2^{ij}g^j + \varrho_s\frac{\partial \hat{f}_s}{\partial \varrho_g}h^i - \varrho_g\frac{\partial \hat{f}_g}{\partial F^{jJ}}F^{-1Ki}G^{jJK}\,, \qquad (72)$$

$$q^i = q_0^i - Q_1^{ij}u^j - Q_2^{ij}g^j\,. \qquad (73)$$

Here, use was made of Eqs (65)–(68) and the symmetry of $\mathbf{G}$; the coefficients k_0^i, q_0^i, K_1^{ij}, K_2^{ij}, Q_1^{ij}, and Q_2^{ij} depend on ϱ_g, $\mathbf{F}$, T, and β.

The inequality (64) is reduced to

$$-T\sigma = \varrho \frac{\partial \hat{f}}{\partial \beta} \dot{\beta} + k_0^i u^i + T^{-1} q_0^i g^i + \left[\varrho_g \left(\frac{\partial \hat{f}_g}{\partial T} + s_{0g}\right) \delta^{ij} - \right.$$

$$\left. - K_2^{ji} - T^{-1} Q_1^{ij}\right] g^i u^j - K_1^{ij} u^i u^j - T^{-1} Q_2^{ij} g^j g^i \leqq 0\,. \qquad (74)$$

The coefficients k_0^i and q_0^i are generally different from zero owing to the first term being different from zero (although they are restricted by the inequality (*74*)). However, in the important case where $\beta = \beta^+$ such that

$$\dot{\beta} = \hat{l}(\varrho_g, \mathbf{F}, T, \beta^+) = 0\,, \qquad (75)$$

it follows from the inequality (*74*) that

$$k_0^i = \hat{k}_0^i(\varrho_g, \mathbf{F}, T, \beta^+) = 0\,, \quad q_0^i = \hat{q}_0^i(\varrho_g, \mathbf{F}, T, \beta^+) = 0\,. \qquad (76)$$

The value of β^+ defined by Eq. (*75*) is the equilibrium value of the internal parameter. The equilibrium in the present simple model is defined as earlier by the conditions (*46*), (*47*), and (*75*). This is again based on zero entropy production, $\sigma = 0$ in the relation (*74*). The result (*76*) is with respect to Eqs (*72*) and (*73*) consistent with Eqs (*50*) and (*51*) (with respect to Eq. (*43*), the last derivative may be written without cross +).

The sufficient condition of equilibrium (minimum of the entropy production) implies certain inequalities for the coefficients in the relation (*74*), *e.g.* positive semidefiniteness of the tensors K_1^{ij} and Q_2^{ij} (for $\beta = \beta^+$; this is related to the choice of the signs in Eqs (*62*) and (*63*), which will be useful in applications[5]).

According to the objectivity principle, also the constitutive equations of the linear model must be isotropic functions (*19*). The constitutive equations for the scalars f_α, f, s_α, s, and $\dot{\beta}$ are according to Eqs (*31*), (*42*), (*55*)–(*57*), and (*71*) isotropic functions of the single "vector" F^{iJ} and scalars ϱ_g, T, β (since any change of the reference system is related only to the space coordinate i; ϱ_s in the functions f and s depends on $\mathbf{F}$ through Eq. (*9*)), hence according to the representation theorem for scalar isotropic functions (ref.[2], appendix D, and ref.[4]), they depend on $\mathbf{F}$ through the "scalar" product, in our case the right Cauchy–Green tensor $\mathbf{C} = \mathbf{F}^T\mathbf{F}$. For example,

$$f_g = \bar{f}_g(\varrho_g, \mathbf{C}, T, \beta)\,. \qquad (77)$$

In the case of ϱ_s, passing from $\mathbf{F}$ to $\mathbf{C}$ is possible thanks to the relation $|\det \mathbf{F}| = \sqrt{(\det \mathbf{C})}$.

The constitutive equations for the vectors $\mathbf{k}$ and $\mathbf{q}$, (72) and (73), are vectorial isotropic functions of $\mathbf{u}$, $\mathbf{g}$, $\mathbf{h}$, $\mathbf{F}$, and $\mathbf{G}$ (the latter two behave as vectors). According to their representation theorem (refs[2,11], Eq. (D 58)), their form is preserved if functions of the type (77) are used in the derivatives (*e.g.* $\partial \hat{f}_g / \partial F^{iJ} = 2(\partial \tilde{f}_g / \partial C^{JK}) F^{iK}$) and the coefficients have the most general form

$$k_0^i = k_{00}^J F^{iJ}, \quad K_r^{ij} = K_{0r}^{JK} F^{iJ} F^{jK} + k_r \delta^{ij}, \tag{78}$$

where k_{00}^J, K_{0r}^{JK}, and k_r (r = 1, 2) are functions of ϱ_g, $\mathbf{C}$, T, and β. Analogous equations apply for q_0^i and Q_r^{ij}.

Isotropic Solid and Fluid

In the above considerations, we did not assume any internal symmetry of the solid s, which could serve us to simplify the constitutive equations. Such a symmetry can be characterized by a symmetry group involving undistinguishable deformations, *i.e.* those which do not change the response of the constitutive equations[2,3].

Consider the most simple case, where the substance s is a nonsimple isotropic material (solid; even fluid may be similar as will be shown below), and a reference configuration exists, which is called undistorted, such that all rotations and inversions are undistinguishable in it[9,10] (compare section 23 in ref.[2]). As follows from the application of the symmetry group of an isotropic nonsimple material, in the corresponding constitutive equations the dependence on $\mathbf{F}$ or $\mathbf{G}$ can be replaced by the dependence on $\mathbf{B}$ or grad $\mathbf{B}$, where $\mathbf{B}$ is the left Cauchy–Green tensor[2,9,10] defined as $\mathbf{B} \equiv \mathbf{F}\mathbf{F}^T$. For example, we obtain from Eqs (56), (57), (72), and (73)

$$f_g = \tilde{f}_g(\varrho_g, \mathbf{B}, T), \quad f_s = \tilde{f}_s(\varrho_g, \mathbf{B}, T, \beta), \tag{79}$$

$$k^i = k_0^i - K_1^{ij} u^j - K_2^{ij} g^j + \varrho_s \frac{\partial \tilde{f}_s}{\partial \varrho_g} h^i - \varrho_g \frac{\partial \tilde{f}_g}{\partial B^{jk}} (\text{grad } \mathbf{B})^{jki}, \tag{80}$$

$$q^i = q_0^i - Q_1^{ij} u^j - Q_2^{ij} g^j. \tag{81}$$

Here, k_0^i, K_r^{ij}, q_0^i, and Q_r^{ij} ($r = 1, 2$) are the same coefficients as in Eqs (72) and (73), but now they are functions of ϱ_g, $\mathbf{B}$, T, and β. In the derivation of Eq. (80) (last term), use was made of the last term in Eq. (72), Eq. (79) (first one) and the identity (ref.[2], Eqs (6.61) and (6.65))

$$G^{iJK} F^{-1Jj} F^{-1Kk} = \tfrac{1}{2}[(\text{grad } \mathbf{B})^{ilk} B^{-1lj} + (\text{grad } \mathbf{B})^{ilj} B^{-1lk} - B^{mi} B^{-1jn} B^{-1kl} (\text{grad } \mathbf{B})^{nlm}]. \tag{82}$$

The above constitutive equations must satisfy again the objectivity principle as expressed by Eq. (*19*). For example, on applying Eq. (*19*) to Eqs (*80*) and (*81*) and rearranging to the form of (*80*) and (*81*) we find that the vectors k_0^i and q_0^i and the tensors K_r^{ij} and Q_r^{ij} (r = 1, 2) are isotropic functions of the variables ϱ_g, $\mathbf{B}$, T, and β. Hence, *e.g.*

$$Q^{ji}k_0^i(\varrho_g, \mathbf{B}, T, \beta) = k_0^i(\varrho_g, \mathbf{QBQ}^T, T, \beta) \qquad (83)$$

for any orthogonal $\mathbf{Q}$, and similarly for $q_0^i(\varrho_g, \mathbf{B}, T, \beta)$. However, according to the representation theorem for isotropic vectorial functions[11] (ref.[2], Eqs (D *58, 59*)), we have for isotropic materials

$$k_0^i \equiv 0\,, \quad q_0^i \equiv 0\,, \qquad (84)$$

since $\mathbf{k}_0$ and $\mathbf{q}_0$ are independent of vector variables. Further,

$$\mathbf{QK}_r(\varrho_g, \mathbf{B}, T, \beta)\, \mathbf{Q}^T = \mathbf{K}_r(\varrho_g, \mathbf{QBQ}^T, T, \beta) \qquad (85)$$

for r = 1, 2 (and analogously for Q_r^{ij}), whence according to the theorems concerning representation of isotropic tensor functions[11] (ref.[2], appendix D) we obtain certain restrictions of the dependence of these coefficients on $\mathbf{B}$ (through representations of symmetrical and antisymmetrical parts of $\mathbf{K}_r$, $\mathbf{Q}_r$).

It can be seen from Eq. (*85*) that for an isotropic material the tensors K_r^{ij} and Q_r^{ij} are reduced to scalars (in the form $\mathbf{K}_r = k_r\mathbf{1}$) only in special cases, *e.g.* for $\mathbf{B} = \alpha^2\mathbf{1}$, *i.e.* in the reference configuration ($\alpha = 1$) or in volume expansion or compression ($\alpha > 1$ or $\alpha < 1$). This follows from the representation theorem for isotropic tensors, which result from Eq. (*85*) if $\mathbf{B}$ is chosen as indicated (*e.g.* ref.[2], Eq. (D *18*)). Namely, an isotropic material remains isotropic during the mentioned "isotropic" deformations starting from the undistorted reference configuration (which is isotropic according to its definition), but not during general deformations. (However, this is not the case with more general materials, *e.g.* K_r^{ij} is not reduced to a scalar even in a reference configuration where $\mathbf{F} = \mathbf{1}$, as can be seen from Eq. (*78*).) The coefficients $\mathbf{K}_r$ and $\mathbf{Q}_r$ are also reduced to scalars in the case of small (infinitesimal) deformations (ref.[1], chapter IX; ref.[2], section 6), when $\mathbf{B} = \mathbf{1} + 2\mathbf{E}$ and $\mathbf{E}$ is the symmetrical part of a small deviation of $\mathbf{F}$ from $\mathbf{1}$. Indeed, terms of the first order involving $\mathbf{E}$ could be involved only in $\mathbf{k}_0$ and $\mathbf{q}_0$, which are however equal to zero according to Eqs (*84*); $\mathbf{K}_r$ and $\mathbf{Q}_r$ are in this approximation independent of $\mathbf{E}$, so that we obtain the preceding case $\alpha = 1$ and, accordingly, these tensor coefficients are reduced to scalars.

For completeness, we shall discuss the case where the material s is also fluid. Its symmetry group is then larger than with isotropic materials and enables us to replace the first and second deformation gradient, $\mathbf{F}$ and $\mathbf{G}$, (with isotropic materials $\mathbf{B}$ and grad $\mathbf{B}$) by the density ϱ_s or its gradient $\mathbf{h}_s \equiv \text{grad}\,\varrho_s$, respectively[2,9]. This was actually done in the preceding sections in the case of the fluid component g. The maximum symmetry group involves the group of the isotropic material, hence use can be made of the results for the isotropic material. Thus, instead of Eqs (*79*) we have

$$f_g = \bar{f}_g(\varrho_g, \varrho_s, T)\,, \quad f_s = \bar{f}_s(\varrho_g, \varrho_s, T, \beta)\,, \tag{86}$$

similarly $f = \bar{f}(\varrho_g, \varrho_s, T, \beta)$ (Eq. (*42*)), and, consequently, $\partial\bar{f}/\partial T = -s$ (Eq. (*31*)). The stress tensor, Eq. (*60*), is reduced to the partial pressure P_s

$$\mathbf{T}_s = -P_s\mathbf{1}\,, \quad P_s \equiv \sum \varrho_\alpha \varrho_s \frac{\partial \bar{f}_\alpha}{\partial \varrho_s} \tag{87}$$

and all coefficients in Eqs (*80*) and (*81*) depend only on the scalars ϱ_g, ϱ_s, T, and β; the last term in Eq. (*80*) is changed to $-\varrho_g(\partial\bar{f}_g/\partial\varrho_s)\,h_s^i$. This follows from the last term in Eq. (*72*), where the derivative will now be equal to $-(\partial\bar{f}_g/\partial\varrho_s)\,\varrho_s F^{-1Ij}$ (since f_g now depends on $\mathbf{F}$ through ϱ_s according to Eq. (*9*)); use is made of Eqs (*6.61*) and (*40.13*) of ref.[2]. The objectivity principle implies that all coefficients in Eqs (*80*) and (*81*) are isotropic tensors, since they depend only on scalars (compare Eqs (*83*) and (*85*), where $\mathbf{B}$ is replaced by the scalar ϱ_s), hence Eqs (*84*) hold good (compare Eqs (D *16*) and (D *18*) of ref.[2]), and other coefficients, which are tensors of the second order, are reduced to scalars. Thus, Eqs. (*80*) and (*81*) for the case where the component s is liquid take the form

$$k^i = -k_1 u^i - k_2 g^i + \varrho_s \frac{\partial \bar{f}_s}{\partial \varrho_g} h^i - \varrho_g \frac{\partial \bar{f}_g}{\partial \varrho_s} h_s^i \tag{88}$$

$$q^i = -q_1 u^i - q_2 g^i\,, \tag{89}$$

where the scalars k_1, k_2, q_1, and q_2 are functions of ϱ_g, ϱ_s, T, and β.

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