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Fundamentals of Surface Thermodynamics

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The nonequilibrium behavior for mixtures of fluids in interfaces is discussed. In particular, a thermodynamic field theory is given for media in thin, curved regions (interfaces with finite thickness), which separates two media with different physical properties. The moving interface is considered as semipermeable and a generalized transport equation and specific balance equations are derived. A systematic investigation of constitutive equations is made and in the limit as the thickness of the interface goes to zero it is shown that all relevant interfacial relations can be found.

1. INTRODUCTION

We study a moving three-dimensional region embedded in and interacting with a three-dimensional continuum. One dimension of the moving region is much smaller than the other two; accordingly, such a thin region can be considered as an interface with finite thickness. This interface can be considered as a model for a membrane. For such an interface we derive a generalized transport equation and specific balance equations for a multiconstituent fluid in heat exchange and material exchange with the bulk fluids. We study the limiting behavior of the transport theorem, the specific balance equations, and the interfacial quantities as the constant thickness ε of the thin region goes to zero. From this limiting process we obtain exact definitions of the surface quantities and interfacial quantities.

Our main interest is to formulate a thermodynamic field theory for discontinuous media with respect to application to a viscous interface and a mixture of fluids in two dimensions with exchange quantities. To that end we find constitutive equations for one viscous fluid in the interface and a mixture of chemically reacting fluids in an interface. By using mathematical

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reduction principles we can restrict the functional form of the constitutive equations. We obtain further restrictions by an entropy principle on the interface (Grauel, 1982a). This entropy principle is physically motivated and it expresses the fact that for all times the entropy production is not a negative quantity, in agreement with physical experience. Moreover, we assume that this principle is valid for all thermodynamic processes, where we consider a thermodynamic process as a solution of the field equations for certain initial and boundary data. The entropy inequality on the interface selects such thermodynamical processes from all possible thermodynamic processes of the field equations that do not violate the entropy inequality. We obtain restrictions. From these restrictions, we obtain surface relation and laws for interfaces by combination of these relations. The integrability condition of some surface relations is used to restrict the list of arguments in the thermodynamic quantities. If we introduce the reduced constitutive equations into the balance equations, we obtain the required field equations for the thermodynamic surface fields.

The use of an entropy principle as a constraint to obtain restrictions for the constitutive equations is accepted in mathematical physics and theoretical thermodynamics. To discuss the nonequilibrium behavior of interfaces, several authors start with the Gibbs equation and combine this equation with the balance equations. In our approach, the Gibbs equation on curved interfaces follows as a logical consequence from an entropy inequality. Let us now specify the features of our approach.

2. PRELIMINARIES

There is an extensive literature on the geometry of surfaces (e.g., Eisenhardt, 1947; Truesdell and Toupin, 1960); McConnell, 1957; Kobayashi and Nomizu, 1963; the geometry of parallel surfaces was treated by Thomas (1965). Here we give two extensions: the surface geometry is time dependent and the thin region is semipermeable. In the next two subsections, I assemble some basic formulas of the geometry of parallel surfaces.

2.1. Surface Geometry

Let us consider a smooth surface $\Sigma(t)$ in the Euclidean space E^3 with a set of orthonormal base vectors $\mathbf{b}_1, \mathbf{b}_2, \mathbf{b}_3$. The position vector $\mathbf{r}$ of any point $P(u^1, u^2, t)$ on a moving surface $\Sigma^0(t)$ can be written in vector form

$$\mathbf{r} = \mathbf{b}_i x^i, \qquad i = 1, 2, 3 \tag{1}$$

where

$$x^i = \chi^i(u^A, t), \qquad A = 1, 2 \tag{2}$$

The u^A are curvilinear coordinates, called surface coordinates on $\Sigma^0(t)$, the surface of reference, and t represents time. Throughout we use covariant notation and the summation convention. The quantity $d\mathbf{r}$ on a point $P(u^1, u^2, t)$ directed tangentially to the u^B-coordinate curve is

$$d\mathbf{r} = \frac{\partial \mathbf{r}}{\partial u^B}\, du^B \tag{3}$$

where

$$\frac{\partial \mathbf{r}}{\partial u^B} = \mathbf{b}_i \frac{\partial x^i(u^A, t)}{\partial u^B} =: \mathbf{a}_B$$

and (3) in component form is

$$dx^i = x^i_{,B}\, du^B \tag{4}$$

The quantities $x^i_{,B}$ are components in space ($i = 1, 2, 3$) lying in the tangent plane on $P(u^1, u^2, t)$ directed tangentially to the surface coordinates u^1 and u^2. The square of the length of arc on $\Sigma(t)$ is given by $(ds)^2 = g_{ij}\, dx^i \otimes dx^j$, and with (4) it follows that

$$(ds)^2 = g_{AB}\, du^A \otimes du^B \tag{5}$$

where $g_{AB} = g_{ij} x^i_{,A} \otimes x^j_{,B}$ is the metric tensor on the surface $\Sigma^0(t)$ and $g_{ij} = \delta_{ij}$ is the metric tensor in space E^3. With g^{AB} denoting the contravariant components of g_{AB}, we have

$$g^{AC} g_{CB} = g_{BC} g^{CA} = \delta^A_B \tag{6}$$

where δ^A_B is the usual Kronecker delta and $C^A = g^{AB} C_B$ and $C^A = \delta^A_B C^B$. The quantities $\mathbf{a}_B$ are base vectors on the surface, together with the normal vector

$$\mathbf{e} = \frac{\mathbf{a}_1 \times \mathbf{a}_2}{|\mathbf{a}_1 \times \mathbf{a}_2|} \tag{7}$$

perpendicular to $\Sigma(t)$. The $(\mathbf{a}_B, \mathbf{e})$ represents a basis on the surface. Equation (7) written in components has the representation

$$e_i = \tfrac{1}{2} \varepsilon^{AB} \varepsilon_{ijk} x^j_{,A} \otimes x^k_{,B} \tag{8}$$

where the ε-tensor in space is denoted by ε_{ijk} and ε^{AB} is the contravariant form of the ε-tensor on surfaces defined similarly as the ε-tensor in space. One has

$$\varepsilon^{AB} = g^{-1/2} \in^{AB} \qquad \text{or} \qquad \varepsilon_{AB} = g^{1/2} \in_{AB} \tag{9}$$

and

$$\varepsilon^{AB} \varepsilon_{CB} = \delta^A_C$$

where δ^A_C is the Kronecker delta on surfaces, $g = \det(g_{AB})$, and $\in_{AB}$ and $\in^{AB}$ are two-dimensional permutation symbols with the properties $\in_{12} = -\in_{21} = 1$, $\in^{12} = -\in_{21} = 1$, and $\in_{11} = \in_{22} = \in^{11} = \in^{22} = 0$. From (8) we conclude that

$$e_i e^i = 1 \qquad \text{and} \qquad e_i x^i{}_{,A} = 0 \tag{10}$$

hold at all times t. With the definition

$$b_{AB} = -x^i{}_{,A} \otimes e_{i,B} \tag{11}$$

of the curvature tensor we obtain by differentiating (10)

$$b_{AB} = e_i \otimes x^i{}_{;AB} \tag{12}$$

where $x^i{}_{;AB} = x^i{}_{,AB} - x^i{}_{,C} \cdot \Gamma^C_{AB}$ is the covariant derivative of $x^i{}_{,C}$ and Γ^C_{AB} is the Christoffel symbol on surfaces. From (11) it follows that $e^i{}_{,A} = -b^C_A x^i{}_{,C}$, where $b^C_A = g^{CB} b_{BA}$. The curvature tensor b_{AB} has scalar invariants

$$k_M = \tfrac{1}{2} \operatorname{tr}(b^A_B) = \tfrac{1}{2} b^A_A \qquad \text{and} \qquad k_G = \det(b^A_B) \tag{13}$$

The derivatives of k_M and k_G with respect to the curvature tensor are

$$\frac{\partial k_M}{\partial b_{CD}} = \tfrac{1}{2} g^{CD} \qquad \text{and} \qquad \frac{\partial k_G}{\partial b_{BC}} = 2k_M g^{BC} - b^{BC} \tag{14}$$

where we have used

$$b^C_A b^A_B = 2k_M b^C_B - k_G \delta^C_B \tag{15}$$

which follows from the Hamilton-Cayley theorem. The derivatives of some surface quantities with respect to time t are given by

$$\left.\frac{\partial x^i{}_{,A}}{\partial t}\right|_{u_B} = (\partial_t x^i)_{,x}|_{u_B} = (ve^i)_{,A}|_{u^B} = v_{,A} e^i + v e^i{}_{,A} \tag{16a}$$

or

$$\left.\frac{\partial x^i{}_{,A}}{\partial t}\right|_{u^B} = v_{,A} e^i - v b^C_A x^i{}_{,C} \tag{16b}$$

where we have defined $\mathbf{v}(u^A, t) = v\mathbf{e}$. Moreover, the following hold:

$$\left.\frac{\partial g_{AB}}{\partial t}\right|_{u^C} = 2v b_{AB} \tag{17}$$

$$\left.\frac{\partial g}{\partial t}\right|_{u^C} = -4g k_M v \tag{18}$$

$$\left.\frac{\partial e_i}{\partial t}\right|_{u^C} = -g^{AB} v_{,B} x_{i,A} \tag{19}$$

$$\left.\frac{\partial b_{AB}}{\partial t}\right|_{u^C} = v_{;AB} - 2k_M v b_{AB} + k_G v g_{AB} \tag{20}$$

Furthermore, we use the following decomposition for the components of a velocity field:

$$w^j = we^j + w^A x^j{}_{,A}$$

2.2. Geometry of Parallel Surfaces

In this subsection we generalize the formulas of the surface in space to a concept of parallel surfaces in space. We consider a smooth surface $\Sigma^0(t)$ and erect the normal N to $\Sigma^0(t)$ in the direction of the unit normal **e** to $\Sigma^0(t)$. We denote by $\Sigma^\xi(t)$ the surface, smooth by hypothesis, obtained by laying off equal distances ξ along the normals N to $\Sigma^0(t)$. Therefore $\Sigma^\xi(t)$ is to be parallel to the surface $\Sigma^0(t)$. The surface $\Sigma^\xi(t)$ is determined by

$$\Sigma^\xi(t): \qquad \mathbf{R} = \mathbf{r} + \xi \mathbf{b}_i e^i, \qquad i = 1, 2, 3 \tag{21}$$

where **R** is the position vector of any point $Q(u^1, u^2, t)$ on the moving surface $\Sigma^\xi(t)$ and **r** is defined by (1). Written in components, this is

$$\Sigma^\xi(t): \qquad \kappa^i = \chi^i(u^A, t) + \xi \cdot e^i(u^A, t), \qquad A = 1, 2 \tag{22}$$

Varying the distance ξ in (22), it is evident that any two surfaces must be parallel and we speak of $\Sigma^\xi(t)$ as a family of parallel surfaces. Formally, $\xi \in [\xi_1, \xi_2]$, where $0 > \xi_1 > -\infty$ and $0 < \xi_2 < \infty$. In a later section we derive balance equations and we consider ξ_1 and ξ_2 as unspecified quantities, which are suitable chosen to describe a membrane of finite thickness. The two surfaces $\Sigma^{\xi_1}(t)$ and $\Sigma^{\xi_2}(t)$ are written briefly $\Sigma^1(t)$ and $\Sigma^2(t)$, which are determined by

$$\Sigma^1(t): \qquad \kappa^i = \chi^i(u^A, t) + \xi_1 \cdot e^i(u^A, t) \tag{23}$$

$$\Sigma^2(t): \qquad \kappa^i = \chi^i(u^A, t) + \xi_2 \cdot e^i(u^A, t) \tag{24}$$

The middle surface between $\Sigma^1(t)$ and $\Sigma^2(t)$ is defined by the representation (2) and we consider this surface as a reference surface in the sense that all geometrical quantities of any surface $\Sigma^\xi(t)$ are expressible in terms of the basic invariants of the reference surface $\Sigma^0(t)$. In the following, I cite some basic formulas of the geometry of parallel surfaces for later application. For a detailed account of the time-dependent geometry of parallel surfaces and shells, see Grauel (1982b). From the concept of parallel surfaces it follows that e_i, the covariant components of the unit normal to $\Sigma^0(t)$ at any point $P(u^1, u^2, t)$, are equal to the covariant components of e_i at point $Q(u^A, t)$ on $\Sigma^\xi(t)$, where Q is the crossing point of the normal N on $P(u^1, u^2, t)$ and $\Sigma^\xi(t)$. Therefore, we do not distinguish between e_i on $\Sigma^0(t)$ and e_i on $\Sigma^\xi(t)$. At any point on $\Sigma^\xi(t)$ we may compute the components of tangent vectors similar to derivatives of (2),

$$\kappa^i{}_{;A} = \chi^i{}_{;A} + \xi \cdot e^i{}_{;A} = (\delta^B_A - \xi \cdot b^B_A)\chi^i{}_{;B} \tag{25}$$

A semicolon denotes covariant differentiation, and a comma denotes partial differentiation in the following. At every point on the interface

$$\kappa^{i}{}_{;A}e_i = 0 \qquad \text{for all} \quad t \tag{26}$$

At the point Q there exist the components $G_{AB} = \kappa^{i}{}_{;A} \otimes \kappa_{i;B}$ of the metric tensor expressed in terms of the basic invariants at the point P on the reference surface, namely

$$G_{AB} = (1 - \xi^2 k_G) g_{AB} - 2\xi(1 - \xi k_M) b_{AB} \tag{27}$$

where k_M and k_G are the mean and the Gaussian curvature. For the metric tensor G_{AB} we may compute the inverse G^{AB} such that

$$G_{AB} G^{BC} = \delta^C_A \tag{28}$$

where δ^C_A is the Kronecker delta. The curvature tensor $B_{AC} = -e^{i}{}_{;A} \otimes \kappa_{i;C}$ in terms of the basic invariants of the reference surface is given by

$$B_{AC} = \xi k_G g_{AC} + (1 - \xi k_M) b_{AC} \tag{29}$$

The scalar invariants on the interface, namely the mean curvature $K_M = \frac{1}{2}$ trace (B_{AC}) and the Gaussian curvature $K_G = \det(B_{AC})$, are given by the equations

$$K_M = \frac{k_M - \xi k_G}{F(\xi)} \tag{30}$$

$$K_G = \frac{k_G}{F(\xi)} \tag{31}$$

where $F(\xi) = \det(\delta^A_C - \xi \cdot b^A_C)$, or by

$$F(\xi) = 1 - 2\xi k_M + \xi^2 k_G \tag{32}$$

In the limit $\xi \to 0$ we have

$$\lim_{\xi \to 0} K_M = k_M \qquad \text{and} \qquad \lim_{\xi \to 0} K_G = k_G \tag{33}$$

G denotes the determinant of the metric tensor G_{AB} such that

$$G = F^2 g \tag{34}$$

If e^{AB} and e_{AB} are alternating tensors on the interface, then we write

$$e^{AB} = G^{-1/2} \varepsilon^{AB} \qquad \text{and} \qquad e_{AB} = G^{1/2} \varepsilon_{AB} \tag{35}$$

where ε^{AB} and ε_{AB} are surface alternators, which are defined as skew-symmetric matrices with the property $\varepsilon_{12} = \varepsilon^{12} = 1$. With respect to the considerations on surfaces and (34), we obtain the relations

$$e^{AB} = F^{-1} \varepsilon^{AB} \qquad \text{and} \qquad e_{AB} = F \varepsilon_{AB} \tag{36}$$

between the alternating tensors on interfaces and those on the reference surface.

3. BALANCE EQUATIONS

We consider a moving three-dimensional region embedded in and interacting with a three-dimensional continuum. The one dimension of the moving region is much smaller than the other two; accordingly, such a region may be regarded as a thin, moving region. There exist in the literature many studies describing thin regions as shells of a material body. Here we extend the shell theory. First, we consider the thin region as not material (interfacial region). Second, we let the interfacial region in general consist of other materials than the surrounding material, with the possibility of interaction within and between the surroundings and the interfacial material. We take into account heat and material exchange. We consider a body $\mathcal{L}(t)$ with the volume $\mathcal{V}(t)$. We assume that this volume is divided into the volumes $\mathcal{V}^+(t)$ and $\mathcal{V}^-(t)$ by a thin region of parallel surfaces with the body $b(t)$ and the volume $\mathcal{U}(t)$. We have $\mathcal{V}(t)=\mathcal{V}^+(t)\cup\mathcal{V}^-(t)\cup\mathcal{U}(t)$, and the volume $\mathcal{V}(t)$ is bounded by $\partial\mathcal{V}(t)=\partial\mathcal{V}^+(t)\cup\partial\mathcal{V}^-(t)\cup\Omega(t)$. Let Ψ be an additive property of $\mathcal{U}(t)$, so that Ψ_v, the amount of Ψ in a partial volume v of $\mathcal{U}(t)$, is given by

$$\Psi_v=\int_v \psi(x^i,t)\,d\tau \tag{37}$$

where $\psi(x^i,t)$ is the density of Ψ_v. We assume that (37) holds for every partial volume of $\mathcal{U}(t)$; moreover, we assume additivity of (37) to obtain the total amount of Ψ in $\mathcal{U}(t)$. The volume $\mathcal{U}(t)$ is bounded by the surfaces Σ^1 and Σ^2 and the lateral surface Ω. The rate of change of Ψ in $\mathcal{U}(t)$ is given by

$$\frac{d\Psi}{dt}=-\Phi(\Psi)+\mathcal{P}(\Psi)+\mathcal{S}(\Psi) \tag{38}$$

where $\Phi(\Psi)$ is the flux through the surface $\partial\mathcal{U}=\Sigma^1\cup\Sigma^2\cup\Omega$. Here $\mathcal{P}(\Psi)$ is a production term

$$\mathcal{P}(\Psi)=\int_{\mathcal{U}} P\cdot d\tau \tag{39}$$

and it represents the production of Ψ in $\mathcal{U}$, for example, the mass production in $\mathcal{U}$ via chemical reactions, and

$$\mathcal{S}(\Psi)=\int_{\mathcal{U}} S\cdot d\tau \tag{40}$$

is the supply of Ψ, for example, by radiation, in the volume $\mathcal{U}$ from the outside of volume $\mathcal{U}$. Here P and S are densities, namely the production density and the density of supply. The flux $\Phi(\Psi)$ consists of two parts, namely a convective flux $\hat{\Phi}(\Psi)$ and a nonconvective part

$$\int_{\partial\mathcal{U}} \Phi^i \eta_i \, dA \tag{41}$$

where Φ^i is the density of the nonconvective flux through $\partial\mathcal{U}$, dA is a surface element of $\partial\mathcal{U}$, and η_j are the covariant components of a surface vector perpendicular to $\partial\mathcal{U}$. From (37) and (38) we have

$$\frac{d}{dt}\int_{\mathcal{U}} \psi \, d\tau = -\hat{\Phi}(\Psi) + \int_{\partial\mathcal{U}} \Phi^i \eta_j \, dA + \int_{\mathcal{U}} (P+S)\, d\tau \tag{42}$$

Let us now perform the calculation step by step. First we calculate the time derivative of the volume integral (Truesdell and Toupin, 1960) on the left-hand side of (42) and set

$$\frac{d}{dt}\int_{\mathcal{U}} \psi \, d\tau = \int_{\mathcal{U}} \frac{\partial\psi}{\partial t} d\tau + \oint_{\partial\mathcal{U}} \psi \dot{s}^k \eta_k \, dA \tag{43}$$

$\dot{s}^k$ are the components of the velocity on the surface bounding the volume $\mathcal{U}$. We consider the density ψ within $\mathcal{U}(t)$ as a function of the coordinates κ^i given by (22) and the time t. Now we compute the time derivative of ψ with respect to fixed surface coordinates u^A and distance ξ and write

$$\frac{\partial\psi}{\partial t}\bigg|_{u^A,\xi} = \frac{\partial\psi}{\partial t}\bigg|_{\kappa^i} + \frac{\partial\psi}{\partial\kappa^j}\bigg|_t \cdot \frac{\partial\kappa^j}{\partial t}\bigg|_{u^A,\xi} \tag{44}$$

where $(\partial\kappa^j/\partial t)|_{u^A,\xi}$ are the components of the velocity of particles in the surface $\Sigma(t)$. In particular the components of the velocity in $\Sigma^1(t)$ are

$$\underset{1}{\dot{s}}^k := \frac{\partial\kappa^k}{\partial t}\bigg|_{u^A,\xi_1} = we^k|_{u^A,\xi_1} - \xi_1 w_{,B}\chi^k{}_{,C}\, g^{CB} \tag{45}$$

and analogously for $\underset{2}{\dot{s}}^k$ if we change ξ_1 by ξ_2. From equations (44) and (45) we have

$$\frac{\partial\psi}{\partial t}\bigg|_{\kappa^i} = \frac{\partial\psi}{\partial t}\bigg|_{u^A,\xi} - w\frac{\partial\psi}{\partial\xi} + \xi g^{BC} w_{,B}\psi_{,C} \tag{46}$$

where $\partial\psi/\partial\xi$ represents the normal derivative and $\psi_{,C}$ the tangential derivative on an arbitrary surface Σ at the distance ξ from the reference surface

Σ^0. With $d\tau = F(\xi)\, d\xi\, d\sigma$ and some manipulations we obtain

$$\int_{\mathcal{U}(t)} \frac{\partial \psi}{\partial t}\, d\tau = \int_{\Sigma^0} \int_{\xi_1}^{\xi_2} \left\{ \frac{\partial \psi}{\partial t}\bigg|_{u^A,\xi} - w \frac{\partial \psi}{\partial \xi}\bigg|_{u^A,\xi} + (\xi g^{BC} w_{,B} \psi_{,C})\big|_{u^A,\xi} \right\} F(\xi)\, d\xi\, d\sigma \tag{47}$$

It is suitable to rewrite the quantity $(\partial\psi/\partial\xi)F(\xi)$ as $\partial(\psi F(\xi))/\partial\xi$ and analogously for the quantities in (47). After some straightforward manipulation on (47) we have

$$\int_{\mathcal{U}(t)} \frac{\partial \psi}{\partial t}\, d\tau = \int_{\Sigma^0} \left\{ \partial_t \underset{s}{\psi} + \frac{\dot g}{2g} \underset{s}{\psi} - w [\![F(\xi)\psi]\!] + w_{;AC} \int_{\xi_1}^{\xi_2} \xi D^{AC}(\xi)\psi\, d\xi + g^{AC} w_{;A} \int_{\xi_1}^{\xi_2} \xi F(\xi)\psi_{,C}\, d\xi \right\} d\sigma \tag{48}$$

where

$$\underset{s}{\psi} = \int_{\xi_1} F(\xi)\psi\, d\xi \tag{49}$$

$$D^{AB}(\xi) = F(\xi) g^{AB} + E^{AB}(\xi) \tag{50}$$

$$E^{AB}(\xi) = -\xi^2 k_G g^{AB} + \xi b^{AB} \tag{51}$$

with the brackets $[\![\cdot]\!]$ we have introduced the jump of the physical quantity ψ on any thin region, which is defined by

$$[\![F(\xi)\psi]\!] = F(\xi_2)\psi|_{\xi_2} - F(\xi_1)\psi|_{\xi_1} \tag{52}$$

$\psi|_{\xi_2}$ is the value of the function $\psi(u^A, \xi, t)$ for $\xi = \xi_2$. The quantity $F(\xi)$ in (52) is defined by (32) and the quantities $F(\xi_1)$ and $F(\xi_2)$ are limiting values of $F(\xi)$ on the surfaces Σ^1 and Σ^2, respectively. The surface integral of (43) has three parts, namely

$$\oint_{\partial\mathcal{U}} \psi \dot s^j \eta_j\, dA = \int_{\Sigma^2} \psi \underset{2}{\dot s}{}^j e_j\, d\Sigma^2 - \int_{\Sigma^1} \psi \underset{1}{\dot s}{}^j e_j\, d\Sigma^1 + \int_{\Omega} \psi \underset{\Omega}{\dot s}{}^j\, d\Omega_j \tag{53}$$

The components of the velocity $\dot s^k$ in the lateral surface $\Omega(t)$ are given by

$$\underset{\Omega}{\dot s} = w e^k + \kappa^k{}_{;A} \dot u^A - \xi w_{,B} \chi^k{}_{,C} g^{BC} \tag{54}$$

where $\dot u^A$ are the components of a velocity in the surface $\Omega(t)$. We refer the interfacial quantities to the reference surface $\Sigma^0(t)$, where the geometrical connection between $\Sigma^1(t)$ or $\Sigma^2(t)$ and $\Sigma^0(t)$ is given by $F(\xi)$, equation

(32). The surface elements are given by $d\Sigma = F(\xi)\, d\sigma$ and $d\Omega_j = D^{EF}\chi_{j,E}\chi_{p,F}n^p\, d\xi\, d\zeta$ (Grauel, 1982b). After some mathematical operations we obtain

$$\oint_{\partial\mathcal{U}} \psi \dot{s}^j \eta_j\, dA = \int_{\Sigma^0} \left\{ w \llbracket F(\xi)\psi \rrbracket + (\underset{s}{\psi}\dot{u}^A)_{;A} - \left(w_{;C} \int_{\xi_1}^{\xi_2} \xi \psi D^{AC}\, d\xi \right)_{;A} \right\} d\sigma \tag{55}$$

and (43) is given by

$$\frac{d}{dt}\int_{\mathcal{U}} \psi\, d\tau = \int_{\Sigma^0} \left\{ \partial_t \underset{s}{\psi} + \frac{\dot{g}}{2g}\underset{s}{\psi} + (\underset{s}{\psi}\dot{u}^A)_{;A} + w_{;A}\psi^A \right\} d\sigma \tag{56}$$

where

$$\psi^A = -\int_{\xi_1}^{\xi_2} [E^{AC}(\xi)\psi_{;C} + D^{AC}(\xi)_{;C}\psi]\xi\, d\xi \tag{57}$$

The nonconvective part of (42) can be expressed by

$$\int_{\partial\mathcal{U}(t)} \Phi^j \eta_j\, dA = \int_{\Sigma^2(t)} \Phi^j e_j\, d\Sigma^2 - \int_{\Sigma^1(t)} \Phi^j e_j\, d\Sigma^1 + \int_{\Omega(t)} \Phi^j\, d\Omega_j \tag{58}$$

where Φ^j is the density of the nonconvective flux through $\partial\mathcal{U}$. With Stokes' theorem, equation (58) takes the form

$$\int_{\partial\mathcal{U}} \Phi^j \eta_j\, dA = \int_{\Sigma^0} \{\llbracket F(\xi)\Phi^j \rrbracket e_j + \Phi^A{}_{;A}\}\, d\sigma \tag{59}$$

and Φ^A is given by

$$\Phi^A =: \chi_{j,B}\int_{\xi_1}^{\xi_2} \Phi^j D^{AB}\, d\xi \tag{60}$$

Now we calculate the convective part of (42),

$$\begin{aligned} \hat{\Phi}(\Psi) = {} & \int_{\Sigma^2(t)} \psi \cdot (v^j - \underset{2}{\dot{s}}{}^j) e_j\, d\Sigma^2 - \int_{\Sigma^1(t)} \psi \cdot (v^j - \underset{1}{\dot{s}}{}^j) e_j\, d\Sigma^1 \\ & + \int_{\Omega(t)} \psi \cdot (v^j - \underset{\Omega}{\dot{s}}{}^j)\, d\Omega_j \end{aligned} \tag{61}$$

$v^j(x^i, t)$ are the components of the velocity in $\mathcal{U}(t)$ and the $\dot{s}^j(x^i, t)$ are defined on the surfaces $\Sigma^1(t)$ and $\Sigma^2(t)$. The $\underset{\Omega}{\dot{s}}{}^j(x^i, t)$ is defined by (54).

Using Stokes' theorem and by some manipulation, we have

$$\hat{\Phi}(\Psi) = \int_{\Sigma^0} \{\llbracket F(\xi)\psi \cdot (v^j - \dot{s}^j) \rrbracket e_j + \hat{\Phi}^A{}_{;A}\}\, d\sigma \tag{62}$$

where

$$\hat{\Phi}^A = \int_{\xi_1}^{\xi_2} \psi \cdot \{(v_j \chi^j{}_{,B} + \xi w_{;B}) D^{AB}(\xi) - F(\xi) \dot{u}^A\} \, d\xi \tag{63}$$

Finally, we have the explicit expression of (42),

$$\begin{aligned} &\int_{\Sigma^0} \left\{ \partial_t \underset{s}{\psi} + \frac{\dot{g}}{2g} \underset{s}{\psi} + (\underset{s}{\psi} \dot{u}^A)_{;A} + w_{;A} \psi^A \right\} d\sigma \\ &\quad = - \int_{\Sigma^0} \{\Phi^A{}_{;A} + \llbracket F(\xi) \Phi^j e_j \rrbracket\} \, d\sigma \\ &\qquad - \int_{\Sigma^0} \{\hat{\Phi}^A{}_{;A} + \llbracket F(\xi) \psi \cdot (v^j - \dot{s}^j) e_j \rrbracket\} \, d\sigma + \int_{\Sigma^0} (p + s) \, d\sigma \end{aligned} \tag{64}$$

The last term in (64) has the simple form

$$\int_{\mathcal{U}} (P + S) \, d\tau = \int_{\Sigma^0} \int_{\xi_1}^{\xi_2} F(\xi) \{P + S\} \, d\xi \, d\sigma = \int_{\Sigma^0} (p + s) \, d\sigma \tag{65}$$

where the production can be written

$$p = \int_{\xi_1}^{\xi_2} F(\xi) P \, d\xi \tag{66}$$

and the supply has the form

$$s = \int_{\xi_1}^{\xi_2} F(\xi) S \, d\xi \tag{67}$$

Equation (64) is valid for arbitrarily small areas on the reference surface and therefore we obtain a local equation of balance

$$\begin{aligned} &\partial_t \underset{s}{\psi} + \frac{\dot{g}}{2g} \underset{s}{\psi} + w_{;A} \psi^A + (\underset{s}{\psi} \dot{u}^A + \Phi^A + \hat{\Phi}^A)_{;A} \\ &\qquad + \llbracket F(\xi) \{\psi \cdot (v^j - s^j) e_j + \Phi^j e_j\} \rrbracket = p + s \end{aligned} \tag{68}$$

which is valid for all points in the thin region. The quantity $\xi = \xi_2 - \xi_1$ is the thickness of the interfacial region and the other quantities are defined by

$$\underset{s}{\psi} = \int_{\xi_1}^{\xi_2} F(\xi) \psi \, d\xi \tag{69a}$$

$$\psi^A = -\int_{\xi_1}^{\xi_2} (E^{AB}(\xi)\psi_{;B} + D^{AB}(\xi)_{;B}\psi)\xi \, d\xi \tag{69b}$$

$$\Phi^A = \chi_{j,B} \int_{\xi_1}^{\xi_2} \Phi^j D^{BA}(\xi) \, d\xi \tag{69c}$$

$$\hat{\Phi}^A = \int_{\xi_1}^{\xi_2} \psi\{D^{AB}(\xi)(v_j\chi^j{}_{,B} + \xi w_{;B}) - F(\xi)\dot{u}^A\psi\} \, d\xi \tag{69d}$$

$$p = \int_{\xi_1}^{\xi_2} F(\xi) P \, d\xi \tag{69e}$$

$$s = \int_{\xi_1}^{\xi_2} F(\xi) S \, d\xi \tag{69f}$$

and

$$D^{AB}(\xi) = F(\xi)g^{AB} + E^{AB}(\xi) \tag{70}$$

$$E^{AB}(\xi) = -\xi^2 k_G g^{AB} + \xi b^{AB} \tag{71}$$

4. SPECIAL EQUATIONS OF BALANCE

In this section we discuss special equations of balance for mixtures of fluids in thin regions that are in heat and material exchange with the surrounding media. To do this we specialize the transport theorem to the balance of mass, momentum, internal energy, and entropy by identifying $\underset{s}{\psi}$, ψ^A, Φ^A, and $\hat{\Phi}^A$ with physical quantities in the thin regions. In a later subsection we study the limiting behavior of the transport theorem (68) and the quantities (69)-(71) to obtain the transport theorem on surfaces and interfaces.

4.1. Equations of Balance for a Mixture of Fluids in a Thin Region (Membrane)

With the definitions in Table I we obtain the equation of mass for δ constituents of fluids in the thin region in the following form:

$$\partial_t \Gamma_\delta + \frac{\dot{g}}{2g}\Gamma_\delta + (\Gamma_\delta \dot{u}_\delta^A + \Delta_\delta^A)_{;A} + \Gamma_\delta^A w_{\delta;A} + [\![F(\xi) \cdot \rho_\alpha \cdot (v_\alpha^j - \dot{s}^j) e_j]\!] = p_\delta \tag{72}$$

Table I. Notation for Mass, Momentum, Energy, and Entropy in a Thin Region

	$\underset{s}{\psi}$	ψ^A	Φ^A	$\hat{\Phi}^A$	p	s
Mass of the constituent δ	Γ_δ	Γ_δ^A	0	Δ_δ^A	π_δ	0
Moment of the constituent δ	$\gamma_\delta \dot{x}_\delta^k$	R_δ^{kA}	$-T_\delta^{kA}$	ζ_δ^{kA}	m_δ^k	$\Gamma_\delta \mathscr{F}_\delta^k$
Energy of the constituent δ	$\gamma_\delta({}_s\varepsilon_\delta + \frac{1}{2}\dot{x}_\delta^k \dot{x}_k^\delta)$	α_δ^A	$-T_\delta^{kA} x_k + Q_\delta^A$	β_δ^A	${}_s e_\delta$	$\Gamma_\delta \mathscr{F}_\delta^k \dot{x}_k^\delta + \Gamma_{\delta s} r_\delta$
Entropy	$\gamma \eta_s$	M^A	Φ^A	N^A	π_s	0

where

$$\Gamma_\delta = \int_{\xi_1}^{\xi_2} F(\xi) \rho_\delta \, d\xi \tag{73a}$$

$$\Gamma_\delta^A = \int_{\xi_1}^{\xi_2} [E^{AB}(\xi) \rho_{\delta,B} - D^{AB}(\xi)_{;B} \rho_\delta] \xi \, d\xi \tag{73b}$$

$$\Delta_\delta^A = \int_{\xi_1}^{\xi_2} \rho_\delta [F(\xi)(v_\delta^A - \dot{u}^A) + v_j \chi^j{}_{,B} E^{AB}(\xi) + \xi w_{\delta;B} D^{AB}(\xi)] \, d\xi \tag{73c}$$

$$p_\delta = \int_{\xi_1}^{\xi_2} F(\xi) \pi_\delta \, d\xi \tag{73d}$$

In these formulas it is assumed that the density of mass $\rho(u^A, \xi, t)$ depends on the surface coordinates u^A, the distance from Σ^0, and time t. Therefore, Γ_δ represents the mean density distribution over the distance ξ. Here p_δ is the production of mass due to chemical reactions and consequently we have one part of the interaction force and a production of energy due to chemical reactions. Let us assume that the number of independent producers of mass is less than λ. The numbers ζ_δ^r are called stoichiometric coefficients and they specify how many molecules of mass m_δ are created in the reaction r. We require that the mass is a quantity conserved in each reaction $r = 1, \ldots, n$. Therefore, there are n equations for n independent chemical reactions. Hence

$$\sum_{\delta=1}^{\lambda} \zeta_\delta^r m_\delta = 0 \tag{74}$$

With respect to the fact that in each reaction r it is possible that a certain constituent can be produced or destroyed, we introduce the quantity z_r as a quantity that depends on the material in the thin region. For the production of mass in the reaction p we have

$$\pi_\delta^r = \zeta_\delta^r m_\delta z_r \tag{75}$$

In a mixture

$$\pi_\delta = \sum_{r=1}^{n} \zeta^r_\delta m_\delta z_r \tag{76}$$

In the following investigations we consider the z_r as quantities that depend on the thermodynamic fields and the curvature properties.

For the balance of momentum we have

$$\begin{aligned} &\partial_t(\gamma_\delta \dot{x}^k_\delta) + \frac{\dot{g}}{2g}\gamma_\delta \dot{x}^k_\delta + w_{;A} R^{kA}_\delta + (\gamma_\delta \dot{x}^k_\delta \otimes \dot{u}^A - T^{kA}_\delta + \zeta^{kA}_\delta)_{;A} \\ &+ [\![F(\xi)\{\rho_\alpha v^k_\alpha \otimes (v^j_\alpha - \dot{s}^j)e_j - t^{kj}_\alpha e_j\}]\!] = \mathscr{m}^k_\delta + \Gamma_\delta \mathscr{F}^k_\delta \end{aligned} \tag{77}$$

where

$$\gamma_\delta \dot{x}^k_\delta = \int_{\xi_1}^{\xi_2} F(\xi)\rho_\delta v^k_\delta \, d\xi \tag{78a}$$

$$R^{kA} = \int_{\xi_1}^{\xi_2} \{E^{AB}(\xi)(\rho_\delta v^k_\delta)_{;B} - D^{AB}(\xi)_{;B}\rho_\delta v^k_\delta\}\xi \, d\xi \tag{78b}$$

$$T^{kA}_\delta = \chi_{j,B} \int_{\xi_1}^{\xi_2} t^{kj}_\delta D^{BA}(\xi) \, d\xi \tag{78c}$$

$$\mathscr{m}^k_\delta = \int_{\xi_1}^{\xi_2} F(\xi) m^k_\delta \, d\xi \tag{78d}$$

$$\Gamma_\delta \mathscr{F}^k_\delta = \int_{\xi_1}^{\xi_2} F(\xi)\rho_\delta f^k_\delta \, d\xi \tag{78e}$$

$$\zeta^{kA}_\delta = \int_{\xi_1}^{\xi_2} \rho_\delta v^k_\delta \otimes \{F(\xi)(v^A_\delta - \dot{u}^A_\delta) + v_j \chi^j{}_{,B} E^{BA}(\xi) + \xi w_{;B} D^{BA}(\xi)\} \, d\xi \tag{78f}$$

We can write for the balance of internal energy

$$\begin{aligned} &\partial_t \gamma_\delta({}_s\varepsilon_\delta + \tfrac{1}{2}\dot{x}^k_\delta \dot{x}^\delta_k) + \frac{\dot{g}}{2g}\gamma_\delta({}_s\varepsilon_\delta + \tfrac{1}{2}\dot{x}^k_\delta \dot{x}^\delta_k) + w_{;A}\alpha^A_\delta \\ &+ [\gamma_\delta({}_s\varepsilon_\delta + \tfrac{1}{2}\dot{x}^k_\delta \dot{x}^\delta_k)\dot{u}^A_\delta + T^{kA}_\delta \dot{x}^\delta_k + Q^A_\delta + \beta^A_\delta]_{;A} \\ &+ [\![F(\xi)\rho_\alpha(\varepsilon_\alpha + \tfrac{1}{2}v^2_\alpha)(v^j_\alpha - \dot{s}^j)e_j - t^{kj}_\alpha v^\alpha_k e_j + q^j_\alpha e_j]\!] \\ &= {}_s e_\delta + \Gamma_\delta \mathscr{F}^k_\delta \dot{x}^\delta_k + \Gamma_\delta \cdot {}_s r_\delta \end{aligned} \tag{79}$$

where

$$Q_\delta^A = \chi_{j,B} \int_{\xi_1}^{\xi_2} q_\delta^j D^{BA}(\xi)\, d\xi \tag{80a}$$

$$T_\delta^{kA} \dot{x}_\delta = \chi_{j,B} \int_{\xi_1}^{\xi_2} t_\delta^{kj} v_k^\delta D^{BA}(\xi)\, d\xi \tag{80b}$$

$$\begin{aligned} \alpha_\delta^A = \int_{\xi_1}^{\xi_2} & \{[D^{AB}(\xi) - F(\xi) g^{AB}][\rho_\delta(\varepsilon_\delta + \tfrac{1}{2} v_\delta^2)]_{;B} \\ & - D^{AB}(\xi)_{;B} \rho_\delta(\varepsilon_\delta + \tfrac{1}{2} v_\delta^2)\} \xi\, d\xi \end{aligned} \tag{80c}$$

$$\begin{aligned} \beta_\delta^A = \int_{\xi_1}^{\xi_2} & \rho_\delta(\varepsilon_\delta + \tfrac{1}{2} v_\delta^2)\{F(\xi)(v_\delta^A - \dot{u}_\delta^A) \\ & + v_j^\delta \chi^j{}_{,B} E^{AB}(\xi) + \xi w_{;B} D^{AB}(\xi)\}\, d\xi \end{aligned} \tag{80d}$$

$$\Gamma_\delta \mathscr{F}_\delta^k \dot{x}_k^\delta = \int_{\xi_1}^{\xi_2} F(\xi) \rho_\delta f_\delta^k v_k^\delta\, d\xi \tag{80e}$$

$$\Gamma_\delta \cdot {}_s r_\delta = \int_{\xi_1}^{\xi_2} F(\xi) \rho_\delta r_\delta\, d\xi \tag{80f}$$

$${}_s e_\delta = \int_{\xi_1}^{\xi_2} F(\xi) e_\delta\, d\xi \tag{80g}$$

The balance of entropy is given by

$$\begin{aligned} & \partial_t(\gamma \eta_s) + \frac{\dot{g}}{2g} \gamma \eta_s + w_{;A} M^A + (\gamma \eta_s \dot{u}^A + \Phi^A + N^A)_{;A} \\ & + [\![F(\xi)\{\rho \eta \cdot (v^j - \dot{s}^j) e_j + \Phi^j e_j]\!] = \pi_s \end{aligned} \tag{81}$$

$$\gamma \eta_s = \int_{\xi_1}^{\xi_2} F(\xi) \rho \eta\, d\xi \tag{82a}$$

$$M^A = \int_{\xi_1}^{\xi_2} [E^{AB}(\xi)(\rho \eta)_{;B} - D^{AB}(\xi)_{;B} \rho \eta] \xi\, d\xi \tag{82b}$$

$$\Phi^A = \int_{\xi_1}^{\xi_2} \chi_{j,B} \Phi^j D^{AB}(\xi)\, d\xi \tag{82c}$$

$$N^A = \int_{\xi_1}^{\xi_2} \rho \eta \{F(\xi)(v^A - \dot{u}^A) + v_j \chi^j{}_{,B} E^{AB}(\xi) + \xi w_{;B} D^{AB}(\xi)\}\, d\xi \tag{82d}$$

$$\pi_s = \int_{\xi_1}^{\xi_2} F(\xi) \pi\, d\xi \tag{82e}$$

4.2. Equations of Balance at Surfaces and Interfaces

We study now the limiting behavior of the quantities (69). To that end, we consider a thin region between two surfaces $\Sigma^1(t)$ and $\Sigma^2(t)$ of constant thickness ε and fix $\xi_1 = -\varepsilon/2$ and $\xi_2 = \varepsilon/2$. We assume:

(i) The surface field $\psi^+(u^A, t)$ is given by the definition

$$\psi^+(u^A, t) := \lim \psi(x^i, t), \qquad x^i \in \mathcal{V}^+(t), \qquad x^i \to x^i \in \Sigma^2(t) \tag{83}$$

and $\psi^-(u^A, t)$ by an analogous definition.

(ii) The limits of integrals over fields exist and are nonvanishing smooth functions of the coordinates u^A and time t. Let $G(u^A, \xi, t)$ be a scalar-valued function; then

$$g(u^A, t) = \lim_{\varepsilon\to 0} \int_{-\varepsilon/2}^{\varepsilon/2} G(u^A, \xi, t)\, d\xi \tag{84}$$

is the scalar-valued field on the surface or interface. Similarly, we introduce vector-valued functions on surfaces and interfaces by

$$f^j(u^A, t) = \lim_{\varepsilon\to 0} \int_{-\varepsilon/2}^{\varepsilon/2} F^j(u^A, \xi, t)\, d\xi \tag{85}$$

The limiting values of equations (32), (50), and (51) are

$$F(0) = 1 \tag{86a}$$

$$D^{AB}(0) = g^{AB} \tag{86b}$$

$$E^{AB}(0) = 0 \tag{86c}$$

and

$$\lim_{\varepsilon\to 0} \int_{-\varepsilon/2}^{\varepsilon/2} \xi^p h(u^A, \xi, t)\, d\xi = 0 \tag{87}$$

where $p > 0$. Therefore $\psi^A = 0$ and (69d) takes the form

$$\hat{\Phi}^A = \lim_{\varepsilon\to 0} \int_{-\varepsilon/2}^{\varepsilon/2} F(\xi)\psi(u^A, \xi, t)(v^A - \dot{u}^A)\, d\xi \tag{88}$$

By definition, the velocity field $\dot{u}^A$ is introduced into the theory independently of certain motions of the particles on the surface Σ^0, and therefore $\hat{\Phi}^A$ represents a diffusion of particles on the surface if we identify $\psi(u^A, \xi, t)$ with the density of mass. If the diffusion flux $\hat{\Phi}^A$ on the surface is zero, we obtain the expression for the velocity field

$$\underset{s}{\psi}\dot{u}^A = \lim_{\varepsilon\to 0} \int_{-\varepsilon/2}^{\varepsilon/2} F(\xi)\psi(u^A, \xi, t)v^A\, d\xi \tag{89}$$

where

$$\underset{s}{\psi}(u^A, t) = \lim_{\varepsilon \to 0} \int_{-\varepsilon/2}^{\varepsilon/2} F(\xi)\psi(u^A, \xi, t)\, d\xi \tag{90}$$

Equation (68) in the limit $\varepsilon \to 0$ has the following form:

$$\partial_t \underset{s}{\psi} + \frac{\dot{g}}{2g}\underset{s}{\psi} + (\underset{s}{\psi} w^A + \Phi^A)_{;A} + [\psi \cdot (v^j - w^j)e_j + \Phi^j e_j] = \pi + \sigma \tag{91}$$

where

$$\Phi^A(u^A, t) := x_{p,B} g^{AB} \lim_{\varepsilon \to 0} \int_{-\varepsilon/2}^{\varepsilon/2} F(\xi)\Phi^p(u^A, \xi, t)\, d\xi \tag{92}$$

$$\pi(u^A, t) := \lim_{\varepsilon \to 0} \int_{-\varepsilon/2}^{\varepsilon/2} F(\xi)P(u^A, \xi, t)\, d\xi \tag{93}$$

$$\sigma(u^A, t) := \lim_{\varepsilon \to 0} \int_{-\varepsilon/2}^{\varepsilon/2} F(\xi)S(u^A, \xi, t)\, d\xi \tag{94}$$

Equation (91) is the same as a result derived earlier (Grauel, 1982a). In that work it was assumed that surface fields exist that are smooth on the surface. Equation (90) shows that the field $\underset{s}{\psi}$ that we obtain by a limiting process depends on the distribution of the density $\psi(u^A, \xi, t)$. Therefore, the surface quantities in (91), have with (90), (93), and (94), a defined meaning by the densities $\psi(u^A, \xi, t)$, $\Phi^j(u^A, \xi, t)$, $P(u^A, \xi, t)$, and $S(u^A, \xi, t)$.

4.2.1. Balance of Mass

Thus we have for the density of mass

$$\gamma_\delta = \lim_{\varepsilon \to 0} \int_{-\varepsilon/2}^{\varepsilon/2} F(\xi)\rho_\delta\, d\xi \tag{95}$$

and for the production of mass

$$\pi_\delta = \lim_{\varepsilon \to 0} \int_{-\varepsilon/2}^{\varepsilon/2} F(\xi)\Pi_\delta\, d\xi \tag{96}$$

Moreover, $\lim_{\varepsilon \to 0} \Gamma_\delta^A = 0$ and the convective flux (73c) is given by $J_\delta^A = \gamma_\delta \cdot (w_\delta^A - \dot{u}^A)$, where

$$w_\delta^A =: \frac{1}{\gamma_\delta} \lim_{\varepsilon \to 0} \int_{-\varepsilon/2}^{\varepsilon/2} F(\xi)\rho_\delta v_\delta^A\, d\xi \tag{97}$$

We have thus

$$\partial_t \gamma_\delta + \frac{\dot{g}}{2g}\gamma_\delta + (\gamma_\delta w_\delta^A)_{;A}[\rho_\alpha \cdot (v_\alpha^j - w_\lambda^j)e_j] = \pi_\delta \tag{98}$$

as the equation of balance for the density of mass in the interface. By a limiting process (Grauel, 1982b) similar to that for the density of mass, we obtain the following equations:

4.2.2. Balance of Momentum

$$\partial_t(\gamma_\delta w_\delta^k)+\frac{\dot{g}}{2g}\gamma_\delta w_\delta^k+(\gamma_\delta w_\delta^k\otimes w_\delta^A-T_\delta^{kA})_{;A}$$

$$+[\rho_\alpha v_\alpha^k\otimes(v_\alpha^j-w_\lambda^j)e_j-t_\alpha^{kj}e_j]=m_\delta^k+\gamma_\delta F_\delta^k \tag{99}$$

where

$$\gamma_\delta w_\delta^k=\lim_{\varepsilon\to 0}\int_{-\varepsilon/2}^{\varepsilon/2}F(\xi)\rho_\delta v_\delta^k\,d\xi \tag{100a}$$

$$T_\delta^{kA}=g^{BA}\chi_{j,B}\lim_{\varepsilon\to 0}\int_{-\varepsilon/2}^{\varepsilon/2}F(\xi)t_\delta^{kj}\,d\xi \tag{100b}$$

$$m_\delta^k=\lim_{\varepsilon\to 0}\int_{-\varepsilon/2}^{\varepsilon/2}F(\xi)\hat{m}_\delta^k\,d\xi \tag{100c}$$

$$\gamma_\delta F_\delta^k=\lim_{\varepsilon\to 0}\int_{-\varepsilon/2}^{\varepsilon/2}F(\xi)\rho_\delta f_\delta^k\,d\xi \tag{100d}$$

$$\gamma_\delta w_\delta^k\otimes w_\delta^A=\lim_{\varepsilon\to 0}\int_{-\varepsilon/2}^{\varepsilon/2}F(\xi)\rho_\delta v_\delta^k\otimes v_\delta^A\,d\xi \tag{100e}$$

4.2.3. Balance of Internal Energy

$$\partial_t\gamma_\delta({}_sE_\delta+\tfrac{1}{2}w_\delta^2)+\frac{\dot{g}}{2g}\gamma_\delta\cdot({}_sE_\delta+\tfrac{1}{2}w_\delta^2)+(\gamma_\delta({}_sE_\delta+\tfrac{1}{2}w_\delta^2)w_\delta^A-T^{kA}w_k^\delta+Q_\delta^A)_{;A}$$

$$+[\rho_\alpha(\varepsilon_\alpha+\tfrac{1}{2}v_\alpha^2)(v_\alpha^j-w_\lambda^j)e_j-t_\alpha^{kj}v_k^\alpha e_j+q_\alpha^i e_j]$$

$$={}_se_\delta+\gamma_\delta F_\delta^k w_k^\delta+\gamma_\delta\,{}_sr_\delta \tag{101}$$

where

$$\gamma_\delta({}_sE_\delta+\tfrac{1}{2}w_\delta^2)=\lim_{\varepsilon\to 0}\int_{-\varepsilon/2}^{\varepsilon/2}F(\xi)\rho_\delta(\varepsilon_\delta+\tfrac{1}{2}v_\delta^2)\,d\xi \tag{101a}$$

$$-T_\delta^{kA}w_k^\delta+Q_\delta^A=\lim_{\varepsilon\to 0}\chi_{k,B}\int_{-\varepsilon/2}^{\varepsilon/2}F(\xi)g^{AB}\{-t_\delta^{kj}v_j^\delta+q_\delta^k\}\,d\xi \tag{101b}$$

$${}_se_\delta=\lim_{\varepsilon\to 0}\int_{-\varepsilon/2}^{\varepsilon/2}F(\xi)e_\delta\,d\xi \tag{101c}$$

$$\gamma_\delta F^k_\delta w^k_\delta + \gamma_{\delta\ s} r_\delta = \lim_{\varepsilon \to 0} \int_{-\varepsilon/2}^{\varepsilon/2} F(\xi)\{\rho_\delta f^k_\delta v^\delta_k + \rho_\delta r_\delta\}\, d\xi \tag{101d}$$

By some mathematical manipulations using equations (101), we have (Grauel, 1982a)

$$\partial_t(\gamma E_s) + \frac{\dot{g}}{2g}\gamma E_s + (\gamma E_s w^A + Q^A)_{;A} - T^{kA} w_{k;A} + [\rho(\varepsilon + \tfrac{1}{2}(v^k - w^k)^2)$$

$$\times (v^j - w^j_\lambda) + q^j - t^{kj} g_{kl}(v^l - w^l) e_j] = \gamma r_s \tag{102}$$

4.2.4. Balance of Entropy

$$\partial_t(\gamma\eta_s) + \frac{\dot{g}}{2g}\gamma\eta_s + (\gamma\eta_s w^A + \Phi^A)_{;A} + [\rho\eta(v^j - w^j)e_j + \Phi^j e_j] = \pi_s \tag{103}$$

where

$$\gamma\eta_s = \lim_{\varepsilon \to 0} \int_{-\varepsilon/2}^{\varepsilon/2} F(\xi)\rho\eta\, d\xi \tag{104a}$$

$$\Phi^A = \lim_{\varepsilon \to 0} x_{j,B} \int_{-\varepsilon/2}^{\varepsilon/2} \Phi^j D^{AB}(\xi)\, d\xi \tag{104b}$$

Equations (98), (99), (101), and (103) are the same as given by Grauel (1980, 1982a), except that here we have defined the surface quantities precisely.

5. CONSTITUTIVE EQUATIONS FOR SEMIPERMEABLE SURFACES AND INTERFACES

The constitutive equations depend on the physical field variables, namely the density of mass, velocity, temperature, and geometrical field variables used to characterize the curvature properties. If we know the constitutive equations, then these, together with the balance equations, give the field equations for the surface fields.

Definition. Every set of surface fields that yields a solution of the field equations under initial and boundary conditions is called an interfacial thermodynamic process of the material under consideration.

The equations of semipermeable surfaces are the equations of balance of mass, momentum, and internal energy and are given by

$$\begin{gathered}
\partial_t\gamma_\delta+\frac{\dot g}{2g}\gamma_\delta+(\gamma_\delta w_\delta^A)_{;A}+[\rho_\alpha\cdot(v_\alpha^j-w_\lambda^j)e^j]=\sum_{r=1}^{n}\zeta_\delta^r m_\delta z_r\\
\partial_t(\gamma_\delta w_\delta^k)+\frac{\dot g}{2g}\gamma_\delta w_\delta^k+(\gamma_\delta w_\delta^k\otimes w_\delta^A-T_\delta^{kA})_{;A}\\
+[\rho_\alpha v_\alpha^k\otimes(v_\alpha^j-w_\lambda^j)-t_\alpha^{kj}]e^j=m_\delta^k+\gamma_\delta F_\delta^k\\
\partial_t(\gamma E_s)+\frac{\dot g}{2g}\gamma E_s+(\gamma E_s w^A+Q^A)-T^{kA}w_{k;A}\\
+[\rho(\varepsilon+\tfrac{1}{2}(v^k-w^k)^2)(v^j-w_\lambda^j)+q^j-t^{kj}g_{kl}(v^l-w^l)]e_j\\
=\sum_{\delta=1}^{\lambda}\gamma_{\delta\,s}r_\delta+\sum_{\delta=1}^{\lambda}\gamma_\delta F_\delta^k U_\delta^k
\end{gathered}\tag{105}$$

In addition, the fields of the materials occupying $\mathscr{V}^+(t)$ and $\mathscr{V}^-(t)$ will be governed by the field equations of mass, momentum, and internal energy,

$$\begin{gathered}
\partial_t\rho_\alpha+(\rho_\alpha v_\alpha^j)_{,j}=\tau_\alpha\\
\partial_t\rho_\alpha v_\alpha^k+(\rho_\alpha v_\alpha^k\otimes v_\alpha^j-t_\alpha^{kj})_{;j}=m_\alpha^k+\rho_\alpha f_\alpha^k\\
\partial_t(\rho\varepsilon)+(\rho\varepsilon v^j+q^j)_{,j}=t^{kj}v_{k,j}+\rho\cdot r
\end{gathered}\tag{106}$$

where the constitutive equations for t_α^{kj}, m_α^k, and q^k depend on the fields of the mass density ρ_α, velocity v_α^k, and bulk temperature T in a manner characteristic for the bulk materials on each side of the interface.

The constitutive equations from physically motivated assumptions generally have too complicated a field dependence. Therefore, it is significant to ask how we can reduce this dependence of the variables for a material under consideration. Principles that reduce constitutive equations are called reduction principles and we must require that they be compatible with the laws of physics and mathematics. We use two principles with respect to the functional form of the constitutive equations and require that these are unchanged by (i) Galilean transformation and (ii) transformation of the surface coordinates.

Moreover, we use the representations for isotropic functions. The third principle is a physical one, called the entropy principle. The equations of balance (105) must be supplemented by constitutive equations for E_s, η_s, Q^A, Φ^A, and T^{kA} which relate the surface quantities to the fields of mass density $\gamma(u^A, t)$, velocity $w^k(u^A, t)$, and temperature $T_s(u^A, t)$ in a material-dependent manner. We assume that the value of the surface temperature T_s may differ from the limiting values of the bulk temperatures T^+ and T^- at the interface.

We discuss two different materials, a single viscous fluid and a chemically reacting mixture of fluids in the interface. The constitutive quantities for a single viscous fluid may have the functional dependence

$$C = \mathscr{C}(\gamma,\ T_s,\ x^k{}_{,A}T_{s,k},\ g^{AB}w^k{}_{;A}x^j{}_{,B},\ x^k{}_{,A},\ e^k{}_{,A}) \tag{107}$$

where the gradient $g^{AB}w^k{}_{;A}x^j{}_{,B}$ describes a gradient of the velocity field w^k. We do not consider the explicit dependence of the velocity w^k and a gradient of the density of mass, because this dependence would not yield more information. Moreover, we exclude a variable $\dot{T}_s$ in our theory of a viscous interface. But if we want to consider the possibility of thermal wave propagation at finite speeds, we must include the time derivative of T_s in the theory. The second material under consideration is a heat conducting material with the possibility of chemical reactions in mixtures in the interface. For that we consider the functional dependence

$$C = \mathscr{C}(\gamma_\delta,\ T_s,\ \gamma_{\delta,A},\ T_{s,A},\ w^k_\delta,\ x^k{}_{,A},\ e^k{}_{,A}) \tag{108}$$

In both (107) and (108) the components $x^k{}_{,A}$ and $e^k{}_{,A}$ are added to describe the curvature properties of the interface. In the following we develop the theory for a viscous interface and cite some results for a mixture of nonviscous fluids derived in a previous paper (Grauel, 1982a).

5.1. Kinematical Transformation Properties

5.1.1. Restrictions Imposed by Galilean Transformation

We use two spatial frames $\bar{x}^j$ and x^k, which are related by the Galilean transformation

$$\bar{x}^j = Q^{jk}x^k + v^j t \tag{109}$$

where v^j is a time-independent velocity that relates the origin of the two spatial frames and Q^{ij} is a time-independent orthogonal tensor with $Q^{-1jk} = Q^{kj}$ and $\det(Q^{jk}) = \pm 1$. In the following I require that $\det(Q^{jk}) = +1$. A scalar S, the components of a vector V^j, and the components of a tensor T^{jk} are called objective if holds

$$\bar{S} = S, \qquad \bar{V}^j = Q^{jk}V^k, \qquad \bar{T}^{jk} = Q^{jp}Q^{kq}T^{pq} \tag{110}$$

with respect to (109).

We begin by investigating the transformation properties of some geometrical quantities and the fields on surfaces. When the surface motion $x^i(u^A, t)$ is replaced in (109), it is clear that the quantities $x^i{}_{,A}$ are objective quantities,

$$\bar{x}^i{}_{,A} = Q^{ij}x^i{}_{,A} \tag{111}$$

and moreover

$$\bar{e}^i = Q^{ij}e^j \qquad \text{and} \qquad \bar{e}^i{}_{,A} = Q^{ij}e^j{}_{,A} \tag{112}$$

Consequently g_{AB}, b_{AB}, k_M, and k_G are objective scalars with respect to (109). It is easy to conclude that the mass density γ, the surface temperature

T_s, and the surface gradient $T_{s,A}$ are objective scalars with respect to (109). The deformation measure that characterizes a viscous medium is the variable $g^{AB}w^k{}_{;A}x^j{}_{,B}$ in (107). The transformation is given by

$$\begin{aligned}\overline{g^{AB}x^i{}_{;B}w^j{}_{;A}} = Q^{ip}Q^{jq}g^{AB}x^p{}_{;B}e^q(w_{;A}+w^C b_{AB})\\ +g^{DC}g^{AB}x^p{}_{;B}x^q{}_{;C}(w_{D;A}-wb_{DA})\end{aligned} \tag{113}$$

where we have used $w^j{}_{;A}=Q^{jk}w^k{}_{;A}$ and for $w^k{}_{;A}$ the expression

$$w^k{}_{;A}=(w_{;A}+w^C b_{CA})e^q+(w^C{}_{;A}-wb^C_A)x^q{}_{;C} \tag{114}$$

The first part of the right-hand side in (113) is antisymmetrical with respect to p and q. This gives us the motivation to decompose the second part of the right-hand side into a symmetrical and an antisymmetrical part. If we collect together the antisymmetrical parts, then we obtain

$$\overline{g^{AB}x^p{}_{;B}w^q{}_{;A}}=Q^{ip}Q^{jq}(\Delta^{pq}+d^{pq}) \tag{115}$$

with the definitions

$$\Delta^{pq}=g^{AB}x^p{}_{;B}e^q(w_{;A}+w^C b_{AC})+g^{AB}g^{CD}x^{[p}{}_{;B}x^{q]}{}_{;C}(w_{D;A}-wb_{DA}) \tag{116}$$

$$d^{pq}=g^{AB}g^{DC}x^{(p}{}_{;B}x^{q)}{}_{;C}(w_{D;A}-wb_{DA}) \tag{117}$$

If we imagine that the left-hand side of (113) can be decomposed into a symmetrical part $\bar{d}^{ij}$ and an antisymmetrical part $\bar{\Delta}^{ij}$, then we have

$$\bar{d}^{ij}=Q^{ip}Q^{jq}d^{pq} \tag{118}$$

$$\bar{\Delta}^{ij}=Q^{ip}Q^{jq}\Delta^{pq} \tag{119}$$

Equation (116) represents a rigid rotation and therefore Δ^{pq} does not represent a variable in this theory. The quantity (117) is the deformation gradient on surfaces and remains in the list of variables in (107). The list of variables of a viscous fluid depends on

$$\gamma,\ T_s,\ T_{s,A},\ d^{ij},\ x^j{}_{;A},\ \text{and}\ e^j{}_{;A} \tag{120}$$

Moreover, the transformation properties of the constitutive equations in the surface are given by

$$\bar{E}_s=E_s,\qquad \bar{\eta}_s=\eta_s,\qquad \bar{Q}^A=Q^A,\qquad \bar{\Phi}^A=\Phi^A \tag{121}$$

and

$$\bar{T}^{kA}=Q^{kj}T^{jA} \tag{122}$$

with respect to (110). From the condition that the moment of momentum must be conserved in a viscous fluid, which is true of particles without spin, we conclude that

$$T^A=0\qquad\text{and}\qquad e^k\varepsilon_{AB}(T^{[BA]}+T^{(BA)})=0 \tag{123}$$

Moreover, with the properties of ε_{AB} one has $T^{[BA]}=0$ and directly from (109) it follows that

$$\bar{T}^{AB} = T^{AB} \tag{124}$$

5.1.2. *Principle of Material Objectivity in Space*

For any given scalar-valued constitutive quantities (121) and (124) we shall write $\mathscr{F}$, for the time being, and let Ω represent the list (120) of surface variables. The principle of material objectivity in space requires that the constitutive quantities are invariant in form with respect to the transformation (110). Therefore, it is valid that

$$\mathscr{F}(\Omega) = \mathscr{F}(\bar{\Omega}) \tag{125}$$

for any function $\mathscr{F}$. Equation (125) represents a functional equation which has the explicit form

$$\begin{aligned}
&\mathscr{F}(\gamma, T_s, T_{s,B}, d^{jk}, x^j{}_{;A}, e^j{}_{;A}) \\
&\quad = \mathscr{F}(\bar{\gamma}, \bar{T}_s, \bar{T}_{s,B}, \bar{d}^{jk}, \bar{x}^j{}_{;A}\bar{e}^j{}_{;A}) \\
&\quad = \mathscr{F}(\gamma, T_s, T_{s,B}, Q^{jp}Q^{kq}d^{pq}, Q^{jp}x^p{}_{;A}, Q^{jp}e^p{}_{;A})
\end{aligned} \tag{126}$$

The function $\mathscr{F}$ will be a scalar-valued function; therefore $\mathscr{F}$ consists of all possible combinations of scalar products, scalar triple products, etc., which we obtain by a combination of the vector variables, tensor variable d^{jk}, and the scalars of the list Ω. The vector-valued variables are $x^j{}_{;A}$ and $e^j{}_{;A}$. Not all combinations of these variables are independent of each other. We have the following independent products, which yield linear variables

$$\begin{aligned}
x^j{}_{;A} \otimes x^j{}_{;B} &= g_{AB} \\
-x^j{}_{;A} \otimes e^j{}_{;B} &= b_{AB} \\
d^{jk}x^j{}_{;A} \otimes x^k{}_{;B} &= d_{AB}
\end{aligned} \tag{127}$$

where

$$d_{AB} = w_{(A;B)} - wb_{AB} \tag{128}$$

If we neglect multiple products of variables that yield nonlinear scalar-valued terms, we obtain a representation of $\mathscr{F}$ that is linear in the fields γ, T_s, $T_{s,A}$, d_{AB}, g_{AB}, and b_{AB} such that

$$F = \mathscr{F}(\gamma, T_s, T_{s,A}, d_{AB}, g_{AB}, b_{AB})$$

5.1.3. Restrictions Imposed by Transformations of the Surface Coordinates

Obviously, the surface coordinates in the form

$$u^A = u^A(\bar{u}^B) \tag{129}$$

are not unique, and there are infinitely many curvilinear coordinate systems that can be used to locate points on a given surface Σ. We assume that the transformations (129) are invertible, so that

$$\bar{u}^B = \bar{u}^B(u^A)$$

and we require $\det(\partial u^A/\partial \bar{u}^B) = 0$. We call a scalar s, a vector v^A, and a tensor t^{AB} on the surface objective under (129) if

$$\bar{s} = s, \qquad \bar{v}^A = h^A_B v^B, \qquad \bar{t}^{AB} = h^A_C h^B_D t^{CD} \tag{130}$$

where $h^A_B := \partial \bar{u}^A/\partial u^B$. By $h^{-1C}_A = \partial u^C/\partial \bar{u}^A$ we denote the inverse of h^A_B and we have to require that $\det(h^A_B) \neq 0$ holds. Moreover, we have $h^{-1C}_A h^A_B = \delta^C_B$. From this it follows that $\bar{e}^i{}_{,A} = h^{-1B}_A e^i{}_{,B}$ and $\bar{x}^i = h^{-1B}_A x^i{}_{,B}$ and that the metric tensor and the curvature tensor are objective with respect to (130c). Moreover, we see that the mean curvature k_M and the Gaussian curvature are objective scalars. Let us require that the density γ and the temperature be objective scalars. Whereas the surface gradient of the temperature and the velocity gradient are objective quantities, according to the transformation rule for covariant vectors and tensors:

$$\bar{T}_{s,A} = h^{-1B}_A T_{s,B} \qquad \text{and} \qquad \bar{d}_{AB} = h^{-1C}_A h^{-1D}_B d_{CD} \tag{131}$$

Now we investigate which restrictions follow if we require that the constitutive functions be invariant in form under transformation of the surface coordinates. For the time being we consider $\varphi(s, v_A, t_{AB})$ a constitutive function depending on a scalar s, a covariant vector v_A, and a covariant tensor t_{AB} and let ϕ and $\bar{\phi}$ be the values of this function in the system of coordinates u^A and $\bar{u}^B$; then we require

$$\bar{\phi} = \phi \tag{132a}$$

according to (130a). If

$$\varphi(s, v_A, t_{AB}) = \varphi(\bar{s}, \bar{v}_A, \bar{t}_{AB}) \tag{133}$$

then we have invariance in form and a functional equation

$$\varphi(s, v_A, t_{AB}) = \varphi(s, h^{-1G}_A v_G, h^{-1G}_A h^{-1H}_B t_{GH}) \tag{134a}$$

from which we can conclude scalar-valued invariants. Similarly, we have for a vector-valued or tensor-valued constitutive function

$$\bar{\Psi}^K = h^K_A \Psi^A \tag{132b}$$

$$\bar{\Xi}^{KL} = h^K_A h^L_B \Xi^{AB} \tag{132c}$$

Therefore, we have

$$h^K_C\varphi^C(s, v_A, t_{AB}) = \varphi^K(s, h^{-1G}_A v_G, h^{-1G}_A h^{-1H}_B t_{GH}) \qquad (134b)$$

or

$$h^K_C h^L_D \chi^{CD}(s, v_A, t_{AB}) = \chi^{KL}(s, h^{-1G}_A v_G, h^{-1G}_A h^{-1H}_B t_{GH}) \qquad (134c)$$

Applying the above results to (121) and (124), we can write

$$\begin{aligned}
&E_s(\gamma, T_s, T_{s,A}, d_{AB}, g_{AB}, b_{AB})\\
&\quad = E_s(\gamma, T_s, h^{-1G}_A T_{s,G}, h^{-1G}_A h^{-1H}_B d_{GH}, h^{-1G}_A h^{-1H}_B g_{GH}, h^{-1G}_A h^{-1H}_B b_{GH})\\
&\qquad \eta_s(\gamma, \ldots, b_{AB}) = \eta_s(\gamma, \ldots, h^{-1G}_A h^{-1H}_B b_{GH})\\
&\qquad h^K_C Q^C(\gamma, \ldots, b_{AB}) = Q^K(\gamma, \ldots, h^{-1G}_A h^{-1H}_B b_{GH})\\
&\qquad h^K_C \Phi^C(\gamma, \ldots, b_{AB}) = \Phi^K(\gamma, \ldots, h^{-1G}_A h^{-1H}_B b_{GH})\\
&\qquad h^K_C h^L_D T^{CD}(\gamma, \ldots, b_{AB}) = T^{KL}(\gamma, \ldots, h^{-1G}_A h^{-1H}_B b_{GH})
\end{aligned} \qquad (135)$$

The transformation principles on the surface require that the constitutive functions be isotropic functions with respect to the group of transformations h^A_B, from which we now deduce restrictions for the constitutive functions. Equations (135) are equations of functional behavior; this means that a scalar-valued function depends on scalar invariants. The scalar invariants are

$$\begin{gathered}
\gamma, T_s, k_M, k_G, \mathrm{tr}(\mathbf{d}), \mathrm{tr}(\mathbf{d}^2), \mathrm{tr}(\mathbf{bd})\\
T_{s,A}T_{s,B}g^{AB}, T_{s,A}T_{s,B}b^{AB}, T_{s,A}T_{s,B}d^{AB}
\end{gathered} \qquad (136)$$

with respect to the Hamilton–Cayley theorem for symmetrical matrices. For the construction of constitutive equations by polynomials we use the representation theorems of Smith (1965) and obtain

$$\begin{aligned}
&E_s = E_s(\gamma, T_s, k_M, k_G, \mathrm{tr}(\mathbf{d}), \mathrm{tr}(\mathbf{d}^2), \mathrm{tr}(\mathbf{bd}),\\
&\qquad T_{s,A}T_{s,B}g^{AB}, T_{s,A}T_{s,B}b^{AB}, T_{s,A}T_{s,B}d^{AB})\\
&\eta_s = \eta_s(\gamma, \ldots, T_{s,A}T_{s,B}d^{AB})\\
&Q^K = \kappa^{KA}T_{s,A} + \lambda d^{KA}T_{s,A}, \qquad \kappa^{KA} := \kappa g^{AB} + \hat{\kappa}^{AB}\\
&\Phi^K = \varepsilon^{KA}T_{s,A} + \zeta d^{KA}T_{s,A}, \qquad \varepsilon^{KA} := \varepsilon g^{AB} + \hat{\varepsilon} b^{AB}\\
&T^{KL} = Ag^{KL} + Bb^{KL} + Cd^{KL} + DT_{s,A}T_{s,B}g^{B(K}g^{L)A} + ET_{s,A}T_{s,B}g^{B(K}d^{L)A}\\
&\qquad + FT_{s,A}T_{s,B}g^{B(K}b^{L)A} + Gd^{(K}_A b^{L)A}
\end{aligned} \qquad (137)$$

where $\kappa, \hat{\kappa}, \varepsilon, \hat{\varepsilon}, \lambda, \zeta, A, \ldots, G$ depend on the list of variables (136).

5.2. Newtonian Fluid

We now discuss a Newtonian fluid in the interface. To that end we restrict the list of variables to a linear dependence of the thermodynamic variables; in particular the stress in the surface depends linearly on the velocity gradient $d_{AB} = w_{(A;B)} - wb_{AB}$ and terms of the form $g^{AB}T_{s,A}T_{s,B}$ are neglected. The scalar-valued quantities are given by

$$E_s = E_s(\gamma, T_s, k_M, k_G, \mathrm{tr}(\mathbf{d}), \mathrm{tr}(\mathbf{bd}))$$

$$\eta_s = \eta_s(\gamma, \dots, \mathrm{tr}(\mathbf{bd}))$$

The vector-valued quantities have the representation

$$Q^A = (-\kappa^{AB} + \kappa d^{AB})T_{s,B}$$

$$\Phi^A = (\varepsilon^{AB} + \varepsilon d^{AB})T_{s,B}$$

and the stress tensor has the form

$$\begin{aligned} T^{KL} = {} & \sigma g^{KL} + \lambda b^{KL} + \eta d^{KL} + \zeta g^{KL}\,\mathrm{tr}(\mathbf{d}) + \nu b^{KL}\,\mathrm{tr}(\mathbf{d}) \\ & + \xi g^{KL}\,\mathrm{tr}(\mathbf{bd}) + \chi b^{AB}\,\mathrm{tr}(\mathbf{bd}) + \mu d_A^{(K} b^{L)A} \end{aligned}$$

where

$$\kappa^{AB} = \underset{1}{\kappa} g^{AB} + \underset{2}{\kappa} b^{AB} \qquad \text{and} \qquad \varepsilon^{AB} = \underset{1}{\varepsilon} g^{AB} + \underset{2}{\varepsilon} b^{AB}$$

$\underset{1}{\kappa}$, $\underset{2}{\kappa}$, $\underset{1}{\varepsilon}$, and $\underset{2}{\varepsilon}$ are functions of γ, T_s, k_M, k_G, tr(**d**), and tr(**bd**); and κ, ε, σ, λ, η, ζ, ν, ξ, χ, and μ are dependent on γ, T_s, k_M, and k_G.

5.3. Restrictions of the Constitutive Equations by a Surface Entropy Principle

The constitutive equations can be further restricted by a physically motivated principle, namely an entropy principle given by Müller (1973). Moeckel (1974) has given a modification for material interfaces and the extension to arbitrary interfaces is straightforward. Let us now apply the entropy principle in the modified form given by Grauel (1980). We assume:

(i) On the interface there exists an additive quantity called the interface entropy η_s which is balanced by

$$\partial_t(\gamma\eta_s) + \frac{\dot{g}}{2g}\gamma\eta_s + (\gamma\eta_s w^A + \Phi^A)_{;A}[\rho\eta(v^j - w_\lambda^j) + \Phi^j]e_j - \gamma\sigma_{\eta_s} = \pi_{\eta_s} \quad (138)$$

where π_{η_s} is the production of entropy.

(ii) For each thermodynamic process[2] on the interface the production of entropy π_{η_s} cannot be negative; therefore we have

$$\pi_{\eta_s} \geq 0 \tag{139}$$

or

$$\partial_t(\gamma\eta_s) + \frac{\dot{g}}{2g}\gamma\eta_s + (\gamma\eta_s w^A + \Phi^A)_{;A} + \langle\rho\eta(v^j - w^j_\lambda) + \Phi^j\rangle e_j - \gamma\sigma_{\eta_s} \geq 0 \tag{140}$$

The interface entropy η_s is a scalar-valued quantity and the entropy flux Φ^A is a vector-valued quantity on the interface. Both η_s and Φ^A must be given by constitutive equations. Furthermore, the quantities enclosed in the angular brackets must be given by constitutive equations. The specific supply of entropy on the interface is given by the supplies of momentum and internal energy

$$\gamma\sigma_{\eta_s} = a_k F^k \gamma + b r_s \gamma \tag{141}$$

where the scalar-valued coefficient b depends on scalars and scalar-valued invariants; the vector-valued coefficient a_k depends on vector-valued quantities. The entropy inequality (140) takes the form

$$\begin{aligned} \partial_t(\gamma\eta_s) &+ \frac{\dot{g}}{2g}\gamma\eta_s + (\gamma\eta_s w^A + \Phi^A)_{;A} \\ &+ [\rho\eta(v^j - w^j_\lambda) + \Phi^j]e_j - (a_k F^k + b r_s)\gamma \geq 0 \end{aligned} \tag{142}$$

Mathematically, each solution of the field equations with respect to initial and boundary data is a thermodynamic process. But we consider only solutions that do not violate the additional restrictive requirement (139) in the form of the entropy inequality (142). Therefore we obtain the required interfacial field $\gamma(u^A, t)$, $w^k(u^A, t)$, and $T_s(u^A, t)$ from the inequality (142) if we take into consideration the field equations as constraints. Liu (1972) has explored these facts in a lemma based on an algebraic equivalence between the system of field equations with (142) as constraint and a new inequality obtained from (142) one introduces into it the field equations multiplied with Lagrange multipliers. Liu has shown that the new inequality is valid without any restriction to the space dimension and that it holds for

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[2] The constitutive equations together with the equations of balance (balance of mass density, balance of momentum, and balance of internal energy) represent the field equations for the fields, namely the field of the density γ, the velocity w^k, and the temperature T_s. A thermodynamic interfacial process is mathematically defined as follows: Each solution of the field equations with respect to initial and boundary data is called a thermodynamic process.

analytical fields. I use this algebraic equivalence and obtain the new inequality in the form

$$
\begin{aligned}
&\partial_t(\gamma\eta_s)+\frac{\dot{g}}{2g}\gamma\eta_s+(\gamma\eta_s w^A+\Phi^A)_{;A}+[\rho\eta(v^j-w^j)+\Phi^j]e_j-a_kF^k\gamma-br_s\gamma\\
&\quad-\Lambda^{\gamma}\Bigg(\partial_t\gamma+\frac{\dot{g}}{2g}\gamma+(\gamma w^A)_{;A}+[\rho_\sigma(v^j_\sigma-w^j)e_j]\Bigg)\\
&\quad-\Lambda^{w}\Bigg(\partial_t(\gamma w)+\frac{\dot{g}}{2g}\gamma w+(\gamma w w^A)_{;A}+\gamma w_{,B}w^B+\gamma w^A\otimes w^B b_{AB}\\
&\quad-T^A{}_{;A}-T^{AB}b_{AB}+[\rho_\sigma v^k_\sigma\otimes(v^j_\sigma-w^j)e_j-t^{kj}_\sigma e_j]e_k-\gamma F\Bigg)\\
&\quad-\Lambda^{w^B}\Bigg(\partial_t(\gamma w^B)+\frac{\dot{g}}{2g}\gamma w^B+(\gamma w^A\otimes w^B)_{;A}-\gamma w w^A b^B_A-\gamma w g^{AB}w_{,A}\\
&\quad-\gamma w\delta^B_A w^C b^A+T^A b^B_A-T^{BA}{}_{;A}+[\rho_\sigma v^k_\sigma\otimes(v^j_\sigma-w^j)e_j-t^{kj}_\sigma e_j]g^{AB}x_{k,A}-F^B\Bigg)\\
&\quad-\Lambda^{E_s}\Bigg(\partial_r(\gamma E_s)+\frac{\dot{g}}{2g}\gamma E_s+(\gamma E_s w^A+Q^A)_{;A}-T^{kA}w_{k;A}\\
&\quad+[\rho(\varepsilon+\tfrac{1}{2}(v^k-w^k)^2)(v^j-w^j)e_j+q^je_j-t^{kj}(v_k-w_k)e_j-\gamma r_s\Bigg)\geq 0 \qquad (143)
\end{aligned}
$$

This entropy inequality must be valid for all thermodynamic fields $\gamma(u^A, t)$, $w^k(u^A, t)$, and $T_s(u^A, t)$. At this moment we are not interested in calculating these fields. However, we are interested in finding further restrictions for the constitutive equations (137). The entropy inequality (143) contains five Lagrange factors, namely the scalar-valued factors Λ^γ, Λ^w, and Λ^{E_s} and the vector-valued factor Λ^{w^B}. These factors can depend on

$$\gamma,\ T_s,\ T_{s,A},\ d_{AB},\ g_{AB},\ \text{and}\ b_{AB}$$

according to the principle of equipresence of Truesdell and Toupin (1960). In particular these factors can depend on the same set of variables as the constitutive equations for scalar-valued or vector-valued quantities.

If we introduce the constitutive equations (137) into the entropy inequality (143) and perform all differentiations step by step, then we obtain an inequality that is linear in the derivatives

$$
\begin{gathered}
\partial_t w,\ \partial_t w^B,\ \partial_t\gamma,\ \partial_t T_s,\ \partial_t T_{s,A},\ \partial_t d_{AB},\ w_{;BA},\ \gamma_{,A}\\
T_{s,(BA)},\ d_{BC,A},\ \text{and}\ b_{BC;A} \qquad (144)
\end{gathered}
$$

The inequality (143) holds for the analytic fields γ, w, w^A, and T_s and it must hold for arbitrary values of derivatives of these fields. The inequality could be violated by an arbitrary choice of values of these fields unless the coefficients of the quantities (144) are identically zero. From this we conclude that the following conditions must be satisfied:

$$\{\partial_t w\}: \qquad \Lambda^{w} = 0 \tag{145}$$

$$\{\partial_t w^B\}: \qquad \Lambda^{w^B} = 0 \tag{146}$$

$$\{\partial_t \gamma\}: \qquad \Lambda^{\gamma} = \frac{\partial \gamma\eta_s}{\partial \gamma} - \Lambda^{E_s}\frac{\partial \gamma E_s}{\partial \gamma} \tag{147}$$

$$\{\partial_t T_s\}: \qquad \frac{\partial \eta_s}{\partial T_s} - \Lambda^{E_s}\frac{\partial E_s}{\partial T_s} = 0 \tag{148}$$

$$\{\partial_t T_{s,A}\}: \qquad \frac{\partial \eta_s}{\partial T_{s,A}} - \Lambda^{E_s}\frac{\partial E_s}{\partial T_{s,A}} = 0 \tag{149}$$

$$\{\partial_t d_{AB}\}: \qquad \frac{\partial \eta_s}{\partial d_{AB}} - \Lambda^{E_s}\frac{\partial E_s}{\partial d_{AB}} = 0 \tag{150}$$

$$\{w_{;BC}\}: \qquad \frac{\partial \eta_s}{\partial b_{AB}} - \Lambda^{E_s}\frac{\partial E_s}{\partial b_{AB}} = 0 \tag{151}$$

$$\{\gamma_{,A}\}: \qquad \frac{\partial \Phi^{A}}{\partial \gamma} - \Lambda^{E_s}\frac{\partial Q^{A}}{\partial \gamma} = 0 \tag{152}$$

$$\{T_{s,(AB)}\}: \qquad \frac{\partial \Phi^{(A}}{\partial T_{s,B)}} - \Lambda^{E_s}\frac{\partial Q^{(A}}{\partial T_{s,B)}} = 0 \tag{153}$$

$$\{d_{BC;A}\}: \qquad \frac{\partial \Phi^{A}}{\partial d_{BC}} - \Lambda^{E_s}\frac{\partial Q^{A}}{\partial d_{BC}} = 0 \tag{154}$$

$$\{b_{BC;A}\}: \qquad \frac{\partial \Phi_{A)}}{\partial b_{B(C}} - \Lambda^{E_s}\frac{\partial Q^{A)}}{\partial b_{B(C}} = 0 \tag{155}$$

We remark that there remains a residual entropy inequality, which will be considered later. The residual entropy inequality is linear in the supply of internal energy by radiation and in the supply of momentum. The inequality could be violated by arbitrary values of r_s and F^k unless

$$b = \Lambda^{E_s} \tag{156}$$

and

$$a_k = 0 \tag{157}$$

Consequently it follows that the supply of entropy in (138) is proportional to the supply of radiation and is given by

$$\sigma_{\eta_s} = \Lambda^{E_s} r_s \tag{158}$$

We now perform the interfacial analysis of exploiting the interfacial relations (145)-(155). If we take into account the constitutive equations for a Newtonian fluid (Section 5.2), then we get restrictions of the constitutive equations. Moreover, we obtain an exact interfacial analysis by combination of certain interfacial relations and some conclusions. Because of the symmetry of $T_{s,AB}$ with respect to A and B, the entropy inequality contains only the symmetrical part of

$$\frac{\partial \Phi}{\partial T_{s,B}} - \Lambda^{E_s} \frac{\partial Q^A}{\partial T_{s,B}} \tag{159}$$

We conclude from the representation of Φ^A and Q^A that (159) has no antisymmetrical part, and with respect to the algebraic independence of the surface tensors g^{AB}, b^{AB}, and d^{AB} among one another we have

$$\underset{1}{\kappa} = \Lambda^{E_s} \underset{1}{\varepsilon}, \qquad \underset{2}{\kappa} = \Lambda^{E_s} \underset{2}{\varepsilon}, \qquad \underset{3}{\kappa} = \Lambda^{E_s} \underset{3}{\varepsilon} \tag{160}$$

Furthermore,

$$\Phi^A = \Lambda^{E_s} \cdot Q^A \tag{161}$$

From the relations (152)-(155) there follow restrictions for the auxiliary function $\Lambda^{E_s}(\gamma, T_s, T_{s,A}, d_{AB}, g_{AB}, b_{AB})$. If we introduce (161) into (152), we obtain

$$\frac{\partial \Lambda^{E_s}(\gamma, \ldots, b_{AB})}{\partial \gamma} Q^A = 0$$

and if $Q^A \neq 0$, we have

$$\frac{\partial \Lambda^{E_s}(\gamma, \ldots, b_{AB})}{\partial \gamma} = 0 \tag{162}$$

Condition (162) means that the function $\Lambda^{E_s}(\gamma, \ldots, b_{AB})$ does not depend on the density field γ. Moreover, we conclude from (153) and (154) that the independence of $T_{s,B}$ and d_{BC} consequently follows $\Lambda^{E_s}(T_s, g_{AB}, b_{AB})$. Because $\Lambda^{E_s}(\ldots)$ is scalar-valued, we write

$$\Lambda^{E_s}(T_s, k_M, k_G) \tag{163}$$

From (155) we obtain the representation

$$Q^{(A} \left\{ \left(\frac{1}{2} \frac{\partial \Lambda^{E_s}(T_s, \ldots, k_G)}{\partial k_M} + 2k_M \frac{\partial \Lambda^{E_s}(T_s, \ldots, k_G)}{\partial k_G} \right) g^{C)B} - \frac{\partial \Lambda^{E_s}(T_s, \ldots, k_G)}{\partial k_G} b^{C)B} \right\} = 0 \tag{164}$$

where we use

$$\frac{\partial k_M}{\partial b_{CD}}=\frac{1}{2}g^{CD} \qquad \text{and} \qquad \frac{\partial k_G}{\partial b_{CD}}=2k_M g^{CD}-b^{CD}$$

Since the metric tensor g^{AB} and the curvature tensor b^{AB} are algebraically independent of each other, we conclude that $\Lambda^{E_s}(\ldots)$ is not dependent on the Gaussian curvature k_G and the mean curvature k_M:

$$\Lambda^{E_s}(T_s) \tag{165}$$

Next we investigate the interfacial relations that relate the internal energy E_s with the entropy η_s together with the constitutive equations, in order to obtain restrictions for the constitutive equations. To that end we rewrite (151) in terms of derivatives $\partial\eta_s/\partial k_M$ and $\partial\eta_s/\partial k_G$ and similarly for E_s and obtain

$$\frac{\partial\eta_s}{\partial k_G}-\Lambda^{E_s}\frac{\partial E_s}{\partial k_G}=0 \tag{166}$$

$$\frac{\partial\eta_s}{\partial k_M}-\Lambda^{E_s}\frac{\partial E_s}{\partial k_M}=0 \tag{167}$$

Indeed, we obtain restrictions for the interfacial thermodynamic quantities. By differentiating (148) with respect to k_M and differentiating (167) with respect to T_s and subtracting the equations from each other we get

$$\frac{\partial\Lambda^{E_s}}{\partial T_s}\frac{\partial E_s}{\partial k_M}=0$$

and if $\partial\Lambda^{E_s}/\partial T_s \neq 0$, then $\partial E_s/\partial k_M=0$ and

$$E_s(\gamma, T_s, k_G, \mathrm{tr}(\mathbf{d}), \mathrm{tr}(\mathbf{bd}))$$

The interpretation is easy: The internal energy does not depend on the mean curvature k_M but on the present state. The curvature properties of the present state can be characterized by the mean curvature k_M and the Gaussian curvature k_G. Further exploitation of (148), (150), (151), (166), and (167) gives

$$E_s=E_s(\gamma, T_s) \tag{168}$$

and

$$\eta_s=\eta_s(\gamma, T_s) \tag{169}$$

Consequently,

$$\Lambda^{\gamma}=\frac{\partial\gamma\eta_s}{\partial\gamma}-\Lambda^{E_s}\frac{\partial\gamma E_s}{\partial\gamma} \tag{170}$$

From the expression (170) we conclude

$$\Lambda^{\gamma} = \Lambda^{\gamma}(\gamma, T_s) \tag{171}$$

With respect to the foregoing results we conclude that the residual inequality (143) can be written in the form

$$\left\{-\gamma^2\left(\frac{\partial \eta_s}{\partial \gamma} - \Lambda^{E_s}\frac{\partial E_s}{\partial \gamma}\right)g^{AB} + \Lambda^{E_s}T^{AB}\right\}d_{AB} + \frac{\partial \Lambda^{E_s}}{\partial T_s}Q^A T_{s,A} \geq 0 \tag{172}$$

We identify the expression (172) with Σ and consider Σ as the production of entropy in the nonequilibrium state. In the equilibrium E we obtain further restrictions for the stress tensor T^{AB} and some interrelations. Equilibrium is characterized as a thermodynamic process in which all constituents are at rest in one frame of reference, so that velocity components of the velocities in the bulk media or interfacial velocities are constant, and all diffusion fluxes and all relative velocities are zero. Moreover, the temperature is uniform and time-independent for both the bulk materials and the interfacial materials. This means that $T_s = T_+ = T_- = T$. Consequently, no heat flux exists in both the bulk media and the interfacial material, and no exchange of heat between the bulk media and the interface occurs. The production of entropy (172) depends on

$$\gamma,\ T_s,\ T_{s,A},\ d_{AB},\ k_M,\ k_G,\ \mathrm{tr}(\mathbf{d}),\ \mathrm{tr}(\mathbf{bd}) \tag{173}$$

where the dependence on the mean curvature k_M and Gaussian curvature is only implicit. The deformation gradient on interfaces d_{AB} is a symmetrical 2×2 tensor, where three components are independent. Therefore, d_{AB} and $\mathrm{tr}(\mathbf{d})$ are not independent of each other. For the exploitation of (172) it is convenient to perform a decomposition of the deformation gradient into two parts, namely into the trace term and a traceless part $\bar{d}_{AB}$. The traceless part of d_{AB} is given by

$$\bar{d}_{AB} = d_{AB} - \tfrac{1}{2} d^{\,C}_{C} g_{AB} \tag{174}$$

where $d^{\,C}_{C} g_{AB}$ is the trace term. Now we exploit (172) for a Newtonian fluid. We consider the production of entropy in the form

$$\begin{aligned}\Sigma = {} & -\gamma^2\left(\frac{\partial \eta_s}{\partial \gamma} - \Lambda^{E_s}\frac{\partial E_s}{\partial \gamma}\right)d^{\,C}_{C} + \Lambda^{E_s}\{\sigma d^{\,C}_{C} + \lambda\ \mathrm{tr}(\mathbf{bd}) + \eta[\bar{d}_{AB}\bar{d}^{AB} + \tfrac{1}{2}(d^{\,C}_{C})^2] \\ & + \zeta(d^{\,C}_{C})^2 + (\nu + \xi) d^{\,C}_{C}\ \mathrm{tr}(\mathbf{bd}) + \chi[\mathrm{tr}(\mathbf{bd})]^2 \\ & + \mu[\bar{s}_{AB}\bar{d}^{AB} + \tfrac{1}{2} d^{\,C}_{C}\ \mathrm{tr}(\mathbf{bd})]\} + \frac{\partial \Lambda^{E_s}}{\partial T_s}Q^A T_{s,A} \geq 0\end{aligned} \tag{175}$$

where

$$\bar{s}_{AB} = b^{\,C}_{(A} d_{B)C} - \tfrac{1}{2} b^{\,D}_{(E} d_{F)D} g^{EF} g_{AB}$$

The entropy production Σ takes on its minimum, namely zero, at the equilibrium. Necessary conditions for the minimum value of Σ are

$$\left.\frac{\partial \Sigma}{\partial T_{s,A}}\right|_E = 0, \qquad \left.\frac{\partial \Sigma}{\partial X_i}\right|_E = 0, \qquad \left.\frac{\partial \Sigma}{\partial\, \mathrm{tr}(\mathbf{bd})}\right|_E = 0 \tag{176}$$

where X_i represents the three independent quantities of the deformation gradient. From (176a) the trivial condition follows

$$Q^A|_E = 0 \tag{177}$$

i.e., the heat flux on the interface must be zero. The condition (176c) represents a restriction on the scalar-valued coefficient λ, namely

$$\lambda|_E = 0 \tag{178}$$

From (176b) it follows that

$$\sigma|_E = -\gamma^2\left(\frac{\partial E_s|_E}{\partial \gamma} - \frac{\partial (T_s \eta_s)|_E}{\partial \gamma}\right) \tag{179}$$

where we have used the result (Grauel, 1980) $\Lambda^E(T_s)|_E = T_s^{-1}$. If we take the condition (148) at equilibrium and take into account (179), we obtain the Gibbs equation

$$d\eta_s|_E = \frac{1}{T_s}\left[\frac{\partial E_s|_E}{\partial T_s}\, dT_s + \left(\frac{\partial E_s|_E}{\partial \gamma} + \frac{\sigma|_E}{\gamma^2}\right) d\gamma\right] \tag{180}$$

and an integrability condition for $\eta_s|_E$ in the form

$$\frac{d \ln(1/T_s)}{dT_s} = \frac{\dfrac{\partial \sigma|_E}{\partial T_s}}{\gamma^2 \dfrac{\partial E_s|_E}{\partial \gamma} + \sigma|_E} \tag{181}$$

At equilibrium the matrix of the second derivatives must be positive semidefinite. Therefore we can write

$$\begin{pmatrix} \dfrac{\partial^2 \Sigma}{\partial X_i\, \partial X_j} & \dfrac{\partial^2 \Sigma}{\partial X_i\, \partial T_{s,A}} & \dfrac{\partial^2 \Sigma}{\partial X_i\, \partial\, \mathrm{tr}(\mathbf{bd})} \\ & \dfrac{\partial^2 \Sigma}{\partial T_{s,A}\, \partial T_{s,B}} & \dfrac{\partial^2 \Sigma}{\partial T_{s,A}\, \partial\, \mathrm{tr}(\mathbf{bd})} \\ & & \dfrac{\partial^2 \Sigma}{\partial\, \mathrm{tr}(\mathbf{bd})\, \partial\, \mathrm{tr}(\mathbf{bd})} \end{pmatrix} = \text{positive semidefinite} \tag{182}$$

In particular we obtain from the condition $(\partial^2 \Sigma / \partial X_i\, \partial X_j)|_E \geq 0$

$$(2\zeta + \eta)|_E \geq 0 \tag{183}$$

and

$$\eta|_E \geq 0 \tag{184}$$

Furthermore, it follows from $[\partial^2\Sigma/\partial X_i\, \partial\, \mathrm{tr}(\mathbf{bd})]|_E \geq 0$ that

$$[2(\nu+\xi)+\mu]_E \geq 0 \tag{185}$$

The condition $[\partial^2\Sigma/\partial\, \mathrm{tr}(\mathbf{bd})\, \partial\, \mathrm{tr}(\mathbf{bd})]|_E \geq 0$ is restrictive for the scalar-valued coefficient χ; we obtain

$$\chi|_E \geq 0 \tag{186}$$

If we take into account the representation (137), then from $(\partial^2\Sigma/\partial T_{s,A}\, \partial T_{s,B})|_E \geq 0$ the condition follows that the tensor-valued heat conduction coefficient must be greater than or equal to zero:

$$\kappa^{AB}|_E \geq 0 \tag{187}$$

Consequently, from (182)

$$\chi|_E(2\zeta+\eta)|_E \geq [2(\nu+\xi)+\mu]^2|_E \tag{188}$$

6. REVIEW OF A MIXTURE OF CHEMICALLY REACTING FLUIDS

In a previous paper (Grauel, 1982a) we have considered an interface $\Sigma(t)$ with a mixture of λ fluids ($\delta = 1, \ldots, \lambda$), which divide a mixture of ν fluids ($\alpha = 1, \ldots, \nu$) from a mixture of μ fluids ($\beta = 1, \ldots, \mu$). The fluids are heat conducting and inviscid, and it is assumed that the interface is permeable and therefore in heat and material exchange. For the interface we have to calculate $4\lambda + 1$ fields as function of the surface parameters u^1 and u^2 and the time t, namely the partial densities $\gamma_\delta(u^1, u^2, t)$, partial velocities $w_\delta^k(u^1, u^2, t)$, and temperature $T_s(u^1, u^2, t)$. The density of the mixture, the velocity of the mixture, the diffusion velocity, and the relative velocity are defined by

$$\begin{aligned}
\gamma &= \sum_{\delta=1}^{\lambda} \gamma_\delta \\
w^k &= \sum_{\delta=1}^{\lambda} \frac{\gamma_\delta}{\gamma} w_\delta^k \\
U_\delta^k &= w_\delta^k - w^k \\
W_\delta^k &= w_\delta^k - w_\lambda^k, \qquad \delta = 1, \ldots, \lambda - 1.
\end{aligned} \tag{189}$$

We assume that the material of one fluid with the density γ_λ is homogeneously distributed on the interface, whereas $\lambda - 1$ fluids can be exchanged with bulk fluids. For the determination of the $4\lambda + 1$ interfacial fields, we have $4\lambda + 1$ balance equations (105). This system of partial differential equations does not represent a closed system of equations. The system can be closed by supplementing constitutive equations of the form (108). The constitutive equations relate the quantities

$$z_r,\ E_s,\ \eta_s,\ m^k_\zeta,\ q^A,\ \Phi^A,\ T^{kA}_\zeta \tag{190}$$

to the surface fields. The constitutive quantities (190) depend on

$$\Omega = \{\gamma_\delta,\ T_s,\ \gamma_{\delta,A},\ T_{s,A},\ w^k_\delta,\ x^k{}_{,A},\ e^k{}_{,A}\} \tag{191}$$

Therefore, the general form of (190) is given by

$$C = \mathscr{C}(\Omega) \tag{192}$$

Independence of a special system of coordinates requires invariance in the form of (192) with respect to Galilean transformation. Therefore, we require

$$\mathscr{C}(\Omega) = \mathscr{C}(\bar{\Omega}) \tag{193}$$

or

$$C = \mathscr{C}(\Sigma) \tag{194}$$

where

$$\Sigma = \{\gamma_\delta,\ T_s,\ \gamma_{\delta,A},\ T_{s,A},\ W_\delta,\ W^A_\delta,\ g_{AB},\ b_{AB}\} \tag{195}$$

If we take into account restrictions imposed by transformation of the surface coordinates, some simplification with respect to the normal velocity W_δ and the tangential velocity W^A_δ and the fact that the scalar-valued functions depend only on scalar-valued quantities, vector-valued functions on vector-valued quantities, and tensor-valued functions on tensor-valued quantities that are combinations of the list (195), it then follows that

$$z_r = z_r(\gamma_\delta,\ T_s,\ k_M,\ k_G) \tag{196a}$$

$$\varepsilon_s = \varepsilon_s(\gamma_\delta,\ T_s,\ k_M,\ k_G) \tag{196b}$$

$$\eta_s = \eta_s(\gamma_\delta,\ T_s,\ k_M,\ k_G) \tag{196c}$$

$$\mathscr{M}_\delta = \sum_{\zeta=1}^{\lambda-1} M_{\delta\zeta} W_\zeta \tag{196d}$$

$$\mathscr{M}^B_\delta = \underset{1}{m}{}^{BA}_\delta \cdot T_{s,A} + \sum_{\zeta=1}^{\lambda} \underset{2}{m}{}^{BA}_{\delta\zeta} \cdot \gamma_{\zeta,A} + \sum_{\zeta=1}^{\lambda-1} \underset{3}{m}{}^{BA}_{\delta\zeta} \cdot W^\zeta_A \tag{196e}$$

$$q^B = \underset{1}{\kappa}{}^{BA} \cdot T_{s,A} + \sum_{\zeta=1}^{\lambda} \underset{2}{\kappa}{}^{BA}_\zeta \cdot \gamma_{\zeta,A} + \sum_{\zeta=1}^{\lambda-1} \underset{3}{\kappa}{}^{BA}_\zeta \cdot W^\zeta_A \tag{196f}$$

$$\Phi^B = \underset{1}{\varphi}{}^{BA} T_{s,A} + \sum_{\zeta=1}^{\lambda} \underset{2}{\varphi}{}^{BA}_\zeta \cdot \gamma_{\zeta,A} + \sum_{\zeta=1}^{\lambda-1} \underset{3}{\varphi}{}^{BA}_\zeta \cdot W^\zeta_A \tag{196g}$$

$$T^{AB}_\delta = -\sigma_\delta g^{AB} + \tau_\delta b^{AB} \tag{196h}$$

where

$$\begin{gathered}\underset{1}{m}{}_{\delta}^{BA}=\underset{1}{M}{}_{\delta}\cdot g^{BA}+\underset{2}{M}{}_{\delta}\cdot b^{BA},\qquad \underset{2}{m}{}_{\delta\zeta}^{BA}=\underset{3}{M}{}_{\delta\zeta}\cdot g^{BA}+\underset{4}{M}{}_{\delta\zeta}\cdot b^{BA}\\ \underset{3}{m}{}_{\delta\zeta}^{BA}=\underset{5}{M}{}_{\delta\zeta}\cdot g^{BA}+\underset{6}{M}{}_{\delta\zeta}\cdot b^{BA}\end{gathered}\tag{196i}$$

$$\begin{gathered}\underset{1}{\kappa}{}^{BA}=\underset{1}{Q}g^{BA}+\underset{2}{Q}b^{BA},\qquad \underset{2}{\kappa}{}_{\zeta}^{BA}=\underset{3}{Q}{}_{\zeta}\cdot g^{BA}+\underset{4}{Q}{}_{\zeta}\cdot b^{BA}\\ \underset{3}{\kappa}{}_{\zeta}^{BA}=\underset{5}{Q}{}_{\zeta}\cdot g^{BA}+\underset{6}{Q}{}_{\zeta}\cdot b^{BA}\end{gathered}\tag{196j}$$

$$\begin{gathered}\underset{1}{\varphi}{}^{BA}=\underset{1}{\phi}\cdot g^{BA}+\underset{2}{\phi}\cdot b^{BA},\qquad \underset{2}{\varphi}{}_{\zeta}^{BA}=\underset{3}{\phi}{}_{\zeta}\cdot g^{BA}+\underset{4}{\phi}{}_{\zeta}\cdot b^{BA}\\ \underset{3}{\varphi}{}_{\zeta}^{BA}=\underset{5}{\phi}{}_{\zeta}\cdot g^{BA}+\underset{6}{\phi}{}_{\zeta}\cdot b^{BA}\end{gathered}\tag{196k}$$

The scalar-valued coefficients

$$\underset{1}{M}{}_{\delta},\ \underset{2}{M}{}_{\delta\zeta},\ \underset{3}{M}{}_{\delta\zeta},\ \ldots,\ \underset{6}{M}{}_{\delta\zeta},\ \underset{1}{Q},\ \underset{2}{Q},\ \underset{3}{Q}{}_{\zeta},\ \ldots,\ \underset{6}{Q}{}_{\zeta},\ \underset{1}{\phi},\ \underset{2}{\phi},\ \underset{3}{\phi}{}_{\zeta},\ \ldots,\ \underset{5}{\phi}{}_{\zeta},\ \underset{6}{\phi}{}_{\zeta},\ \sigma_{\delta},\ \tau_{\delta}$$

are functions of the scalar-valued variables γ_{δ}, T_s, k_M, and k_G. From the condition that the moment of momentum is a conserved quantity, we obtain

$$\sum_{\delta=1}^{\lambda}\mathcal{M}_{\delta}=0\qquad\text{or}\qquad\sum_{\delta=1}^{\lambda}M_{\delta\zeta}=0\tag{197}$$

$$\sum_{\delta=1}^{\lambda}\mathcal{M}_{\delta}^{B}=0\quad\text{or}\qquad\sum_{\delta=1}^{\lambda}\underset{1}{m}{}_{\delta}^{BA}=0,\quad\sum_{\delta=1}^{\lambda}\underset{2}{m}{}_{\delta\zeta}^{BA}=0,\quad\sum_{\delta=1}^{\lambda}\underset{3}{m}{}_{\delta\zeta}^{BA}=0\tag{198}$$

Moreover, we obtain further restrictions by the entropy principle in the form (140), where

$$\gamma\sigma_{\eta_s}=\sum_{\delta=1}^{\lambda}a_k^{\delta}F_{\delta}^{k}\gamma_{\delta}+br_s\gamma\tag{199}$$

We obtain a similar entropy inequality to (143) with additional quantities a_k^{δ} and b and Lagrangian multipliers $\Lambda^{\gamma_{\delta}}$, $\Lambda^{w_{\delta}}$, $\Lambda^{w_{\delta}^{B}}$, and Λ^{E_s} which depend on γ_{δ}, T_s, $\gamma_{\delta,A}$, $T_{s,A}$, W_{δ}, W_{δ}^{A}, g_{AB}, and b_{AB}. The entropy inequality depends linearly on the derivatives

$$\partial_t w_{\delta},\ \partial_t w^{B}\delta,\ \partial_t\gamma_{\delta},\ \partial_t T_s,\ w_{\lambda,(AB)},\ \gamma_{\delta,(BA)},\ T_{s,(BA)},\ w_{\delta,A}^{B},\ w_{\delta,A},\ b_{CD;A}$$

and it holds for all analytical fields γ_{δ}, w_{δ}, w_{δ}^{A}, and T_s. From this entropy inequality we obtain further restrictions for the constitutive equations (196a)–(196h) with the technique as described in Section 5.3. For more details see Grauel (1982a).

Let us consider the residual inequality Σ as a measure of the production of entropy in a nonequilibrium state. If we require that Σ is linear with respect to $\gamma_{\delta,A}$, then we conclude from Σ that $\underset{2}{\kappa}{}^{BA}_{\zeta} = 0$ in (196f) and

$$\underset{2}{m}{}^{BA}_{\delta\zeta} = g^{BA}\{\partial\sigma_\delta/\partial\gamma_\zeta - \gamma_\delta\, \partial\underset{s}{\mu}_\delta/\partial\gamma_\zeta\} \tag{200}$$

in (196e), where we have introduced the chemical potential $\underset{s}{\mu}_\beta$ without velocity-dependent terms by additional considerations. We find for the constituent β in the mixture

$$\underset{s}{\mu}_\beta = \varepsilon_s - T_s\eta_s + \frac{\sigma}{\gamma} + \sum_{\delta=1}^{\lambda} \gamma\left(\delta_{\delta\beta} - \frac{\gamma_\delta}{\gamma}\right)\frac{\partial(\varepsilon_s - T_s\eta_s)}{\partial\gamma_\delta} \tag{201}$$

or

$$\underset{s}{\mu}_\beta = \frac{\partial\gamma(\varepsilon_s - T_s\eta_s)}{\partial\gamma_\beta} \tag{202}$$

σ is the surface tension, T_s is the surface temperature, and $\varepsilon_s - T_s\eta_s = F$ is the free energy. The residual inequality contains heat flux terms, particle diffusion terms, and the affinity of the chemical reactions in the interface, which couple together in specific transport processes. These couplings together with the positivity of the entropy production yield restrictions on the transport equations, which we will not discuss at the moment. The entropy production Σ takes its minimum in the equilibrium state E. Hence

$$\left.\sum_{\delta=1}^{\lambda} \zeta^r_\delta m_\delta \underset{s}{\mu}_\delta\right|_E = 0 \tag{203}$$

where $r = 1, \ldots, n$. Equation (203) means that the chemical affinity is zero in a mixture in the state E. Furthermore, we find

$$2k_M\sigma_\zeta = -[p_\alpha] \tag{204}$$

From this it follows that the product of mean curvature k_M times surface tension σ_ζ is related to a pressure jump on the interface. Moreover, $\underset{1}{\kappa}{}^{AB} \leq 0$ follows in (196f). Let us put together some results of our theory. The Gibbs relation on the interface is given by

$$d\eta_s = \frac{1}{T_s}\left\{\frac{\partial\varepsilon_s}{\partial T_s}\,dT_s + \sum_{\delta=1}^{\lambda}\left[\frac{\partial\varepsilon_s}{\partial\gamma_\delta} + \frac{1}{\gamma}(\varepsilon_s - T_s\eta_s) - \frac{1}{\gamma}\underset{s}{\mu}_\delta\right]\right\} d\gamma_\delta \tag{205}$$

The internal energy and entropy depend on the interface density of the constituent δ and the interfacial temperature

$$\varepsilon_s(\gamma_\delta, T_s) \tag{206a}$$

$$\eta_s(\gamma_\delta, T_s) \tag{206b}$$

We find for the heat flux and entropy flux the representation

$$q^A = -\underset{1}{\kappa}^{AB} T_{s,B} + \sum_{\zeta=1}^{\lambda-1} \underset{3}{\kappa}_{\zeta}^{AB} W_B^{\zeta} \tag{207}$$

$$\Phi^A = \frac{1}{T_s} q^A - \frac{1}{T_s} \sum_{\delta=1}^{\lambda} \gamma_\delta U_\delta^A \underset{s}{\mu}_\delta \tag{208}$$

Furthermore, the interaction normal to the surface contains in lowest order only one term, namely a friction term

$$\mathcal{M}_\delta = \sum_{\zeta=1}^{\lambda-1} M_{\delta\zeta} \cdot W_\zeta \tag{209}$$

and the interaction tangential to the interface depends on a temperature gradient, a friction term, and we have a dependence over a density gradient of the interfacial tension and the interfacial chemical potential

$$\mathcal{M}_\delta^A = \underset{1}{m}_\delta^{AB} T_{s,B} + \sum_{\zeta=1}^{\lambda-1} \underset{3}{m}_{\delta\zeta}^{AB} W_B^{\zeta} + g^{AB} \sum_{\zeta=1}^{\lambda} \{\partial\sigma_\delta/\partial\gamma_\delta - \gamma_\delta\, \partial\underset{s}{\mu}_\delta/\partial\gamma_\delta\}\gamma_{\zeta,B} \tag{210}$$

Moreover, the partial stress tensor has the representation

$$T_\zeta^{AB} = -\sigma_\zeta(\gamma_\delta, T_s) \cdot g^{AB} \tag{211}$$

and the stress tensor in the mixture is given by

$$\tau^{AB} = -\sigma(\gamma_\delta, T_s) \cdot g^{AB} \tag{212}$$

where

$$\sigma = \sum_{\delta=1}^{\lambda} \sigma_\delta = \gamma \sum_{\delta=1}^{\lambda} \gamma_\delta \frac{\partial(\varepsilon_s - T_s\eta_s)}{\partial\gamma_\delta} \tag{213}$$

7. CONCLUSION

In the present paper, we have investigated a nonequilibrium thermodynamic field theory and have studied thermodynamic processes as well as the nonequilibrium behavior of thin regions and interfaces. Furthermore, we have given a rigorous approach to constitutive equations, for a viscous, heat conducting fluid and for a mixture of chemically reacting fluids that are heat conducting. We have not postulated the Gibbs equation on interfaces, but we have seen that this equation can be deduced from an interfacial entropy principle and integrability conditions on interfaces. The interaction force $\mathcal{M}_\delta^A$ tangential to the interface depends on the scalar-valued coefficient of the surface stress and the chemical potential. Moreover, the scalar-valued coefficient of the interfacial tension of the constituent δ depends only on the density γ_δ and the interfacial temperature T_s if the constitutive equations do not depend on density gradients $\gamma_{\delta,A}$.

The method is not restricted to chemically reacting fluids and viscous fluids and the concept of this field-theoretic approach can be applied to fluid films, interfacial fluid membranes, boundary layers, layered structures (liquid crystals), etc., with the possibility of momentum, heat, and material exchange with the surrounding media. Equation (69) shows that we can take into account density distributions and chemically active materials. By a limiting process $\varepsilon \to 0$ we obtain a closed set of boundary conditions for a moving boundary. This boundary can be semipermeable and chemical reactions can occur in the interfacial fluids. Moreover, the theory in the case $\varepsilon \to 0$ can be applied to phase boundary problems and stability considerations of fluid interfaces.

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