Nonlinear Thermodynamics of Moving Material Surfaces in Electric Fields

H. Wallschläger*
Institute for Mathematical Physics, Mendelssohnstr. 3, D-3300 Braunschweig

Z. Naturforsch. **43a,** 829–846 (1988); received April 13, 1988

A continuum-mechanical formalism is presented for the phenomenological description of moving, curvilinear, material surfaces in electric fields in interaction with volume-phases. In addition to conventional equations (balance and constitutive laws) the explicit use of relations for the surface geometry is introduced. A method to establish nonlinear constitutive equations by tensorial and thermodynamical considerations is proved to be applicable to two-dimensional continua. The resulting equations for boundaries interacting with adjacent volumes are of practical importance for the selfconsistent calculation of boundary values. The physical meaning of the different relations is discussed.

PACS: A0340, A4700, A8265

Key words: Nonlinear irreversible thermodynamics, volume-surface-interaction, moving boundary, electric field.

1. Introduction

This paper is concerned with the thermodynamics of stationary or moving surfaces, e.g. shock fronts, phase boundaries or thin films. The surfaces can be material as in case of soap bubbles, or immaterial, as in case of shock fronts. The characterization of such moving material surfaces within the framework of continuum mechanics includes the specification of mass, momentum, energy densities and the geometrical locus as functions of space and time. All this is provided by the solution of a system of field equations consisting of balance, constitutive, boundary and geometry equations.

The presence of a singular surface S, dividing a volume into two parts (see Fig. 1), has strong effects on the behaviour of the adjacent media and vice versa. Especially in the directions normal to the surface strong inhomogeneities are expected, the strongest of which is the discontinuity at the singular surface. The influence of the bulk media in the zone of inhomogeneity and the surface processes have to be taken into account by nonlinear constitutive equations, at the surface as well as in the volume.

An example, where boundaries move in electric fields, is plasma etching, which is a modern method for fine line patterning (cf. Chapman [1]). Surface theories are also applied in normal wet etching, some calculations having been done by e.g. Kuiken et al. [2], in melting problems, the most famous of which is the Stefan problem [3], and in the propagation of shock fronts (cf. Bowen [4]). Already in antiquity surface treatment was employed when pouring out oil on the sea to smooth the waves.

The problems with a priori given surfaces also belong to the subject. Interfaces in electric fields constitute an interesting class of problems as they give rise to electrokinetic phenomena (see Adamson [5]). The description of immaterial surfaces (i.e. without mass singularity) is included in the formalism presented.

Nonlinear constitutive laws for volume phases have been the subject of many studies, as partly summarized by Müller [6]. Special features are discussed e.g.

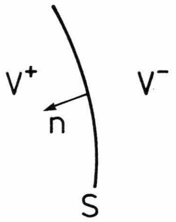

Fig. 1. A singular surface dividing a volume into two parts.

---

* Present address: Institute for Theoretical Physics I, Universitätsstr. 150, D-4630 Bochum.

Reprint requests to Dr. H. Wallschläger, Lehrstuhl I für Theoretische Physik, Ruhr-Universität Bochum, Universitätsstraße 150, D-4630 Bochum.

0932-0784 / 88 / 1000-0829 $ 01.30/0. – Please order a reprint rather than making your own copy.

by Bowen [7] (theory of mixtures) and by Müller et al. [19, 20] (thermodynamics of fluid in electromagnetic fields).

To our knowledge, Waldmann [10] has been the first to discuss a singular surface in a thermodynamic, systematic manner. He transferred the well-known method of linear, irreversible thermodynamics (cf. Meixner and Reik [11]) for obtaining constitutive laws to the two-dimensional case. A sequel of papers followed (e.g. Bedeaux et al. [12], Vodák [13], Kovac [9]). In 1979 Wolff and Albano [14] published a paper concerning the linear characterization of interfaces in electromagnetic fields. All these constitutive equations are examples for linear relations between "fluxes" and "forces", which might become difficult in connection with surfaces. In order to avoid that shortcoming one should transfer the methods of nonlinear thermodynamics to the two-dimensional case. Indeed, Fisher and Leitman [15, 16] started with studies on that subject. Moeckel [17] appears to be the first to treat the problem with mass singularity. We extend these ideas to the case of a mixture in an electric field and stress the physical meaning of the pertaining terms.

Chapter 2 introduces the balance laws for mass, momentum and energy, and Maxwell's equations for volume as well as surface phases. – Chapter 3 is concerned with a new combination of equations in order to give boundary values for the systems treated. – The central subject of this paper is dealt with in Chapt. 4, where we describe the establishment of surface constitutive equations (SCE). In the first part we use some tensorial arguments similar to the well-known "Curie-principle". The second part uses thermodynamic considerations for further simplification of the SCE's. Consequences for the equilibrium state are drawn. – In the final Chapt. 5 we discuss the results. Consequences of the method are set forth and the seemingly abstract terms are interpreted. – As the surfaces in question should be allowed to have a general, time-dependent topology, we give a short summary on the geometry of surfaces embedded in space in the appendix, which also serves as reference for the notation and is related to the work of Aris [8] and Cohen and Wang [18].

2. Equations of Balance

For the description of a physical problem in terms of continuum mechanics one assumes the existence of some densities which give the value of the respective physical quantity by suitable integration. Several descriptions for material surfaces are known:

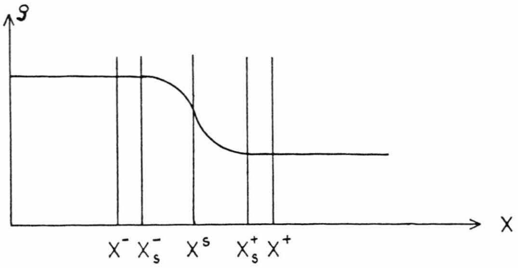

Fig. 2. Example for a material boundary on a microscopic scale. ϱ – Mass density, x^n – coordinate in normal direction.

- According to Adamson [5], Gibbs introduced surface excess densities, as shown in Figure 2. The thermodynamic fields are supposed to be continuous on some microscopic scale in the vicinity of a phase boundary, e.g. An excess density ϱ^s corrects the total density ϱ, calculated by a continuation of the undisturbed volume densities from x^+ resp. x^- to some mathematical surface at x^s. Such excess densities may be positive or negative, having dimensions of volume densities although they are characterizing surfaces. The energetics of the surface may depend, in addition to usual arguments, on the Gaussian and the mean curvatures.
- If a two-dimensional continuum is a good approximation for some boundary region, non-negative surface densities can be introduced for its description. A volume field or its derivatives may suffer a jump at the surface, at least on a microscopic scale. According to Fig. 2, the whole region between x^+ and x^- has to be described as surface, including the region between x^- and x_s^- as well as that between x^+ and x_s^+, which – in a strict sense – belong to the last layers of the respective bulks. This point of view also allows to introduce surface charge densities.

It is this simple concept of non-negative surface densities which is used throughout the present paper.

Figure 3 displays a volume V in the region occupied by the fluid body. This volume may be divided into V^+ and V^- by a surface S, which may happen to be a singular surface S_t. We introduce density fields ψ_V, ψ_S for the physical quantity Ψ with the property

$$\Psi = \int_{V^+ + V^-} \psi_V(x^i, t)\,\mathrm{d}V + \int_S \psi_S(z^A, t)\,\mathrm{d}S\,. \qquad (2.1)$$

With relations given by Aris [8] one is able to establish global balance laws for Ψ. These infer – under suitable

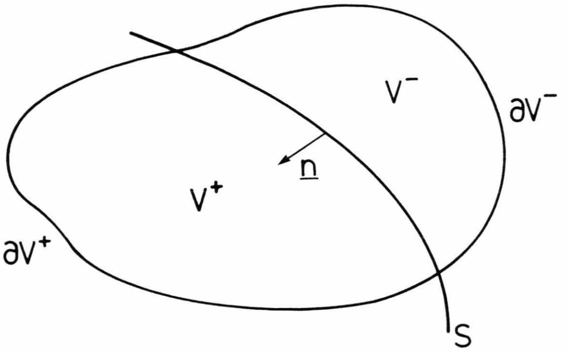

Fig. 3. Regions of integration for the general balance law.

conditions – local balance laws in the volume as well as on S. The general local balance equations are

$$\partial\psi_V/\partial t + (\psi_V\, v^i + \Phi^i_V)_{,i} = p_v + s_v \tag{2.2}$$

for the volume and

$$\partial\psi_S/\partial t - 2K_M\, u\, \psi_S + (\psi_S\, u^A + \Phi^A_S)_{;A} + [\psi_V(v^i - u^i) + \Phi^i_v]\, n_i = p_s + s_s \tag{2.3}$$

for the surface.

In (2.1) and (2.2), Φ^i_V is the nonconvective flux density of ψ_V while p_v and s_v are the respective production- and supply densities. The symbol v^i stands for the mean mass velocity in the volume. Small, Latin indices denote three-dimensional, cartesian coordinates, and Einstein's summation convection is applied. A comma denotes the usual partial derivative. According to (2.2) the evolution of ψ_V is determined by p_v and s_v as well as by the net change of the flux as given by the divergence terms. – Analogously, Φ^A_S is the nonconvective flux density of ψ_S with the respective production- and supply densities p_s and s_s in the surface S, which is localized in the three-dimensional space with help of a parametric representation $x^i = x^i(z^A, t)$, the parameters being the surface coordinates z^A ($A = 1, 2$) and the time t. The vector $\boldsymbol{u}$ stands for the mean mass velocity in the surface and has the cartesian components u^i resp. the tangential components u^A and the normal component u. Capital, Latin indices denote two-dimensional, curvilinear coordinates, and Einstein's summation convention is applied. A semicolon denotes the covariant derivative with respect to the surface coordinates. K_M is the mean curvature of S while n_i stands for the unit normal to the surface. $[L] = L^+ - L^-$ denotes the jump of the volume quantity L, where L^+, L^- indicate the limits of L towards S from V^+, V^-. For details compare with the appendix.

2.1. Volume Equations of Balance

The mass-balances for the ν constituents of a mixture determine the temporal evolution of the partial mass-densities ϱ_α,

$$\partial\varrho_\alpha/\partial t + (\varrho_\alpha\, v^i_{\ \alpha})_{,i} = \tau_\alpha, \quad \alpha = 1, \dots, \nu, \tag{2.4}$$

where $v^i_{\ \alpha}$ is the mass velocity of constituent α and τ_α is the (chemical) mass production density. Small Greek indices number the constituents of a mixture. Summation convection is not applied. Introduction of mass- and momentum-density of the mixture yields the mass-balance for the mixture

$$\partial\varrho/\partial t + v^i\, \varrho_{,i} + \varrho\, v^i_{\ ,i} = 0 \tag{2.5}$$

with

$$\varrho = \sum_{\alpha=1}^{\nu} \varrho_\alpha, \quad \varrho\, v^i = \sum_{\alpha=1}^{\nu} v_\alpha^{\ i}\, \varrho_\alpha, \quad w_\alpha^{\ i} = v_\alpha^{\ i} - v^i,$$

provided the mass production vanishes,

$$\sum_{\alpha=1}^{\nu} \tau_\alpha = 0, \tag{2.6}$$

as follows from the conservation of mass in the mixture.

If the mass production is known in terms of chemical reactions, the production density can be calculated as function of the stoichiometric coefficients γ^a_α and the reaction rate densities Λ^a:

$$\tau_\alpha = \sum_{a=1}^{n} \gamma^a_\alpha\, m_\alpha\, \Lambda^a. \tag{2.7}$$

Obviously there are n reactions between the ν constituents with molecular masses m_α.

The evolution of the mass velocity v^i of the mixture is determined by the balance of momentum

$$\varrho\,(\partial v^i/\partial t + v^j\, v^i_{\ ,j}) - t^{ij}_{\ \ ,j} = \varrho\, f^i. \tag{2.8}$$

In (2.8) the cartesian components of the (mechanical) stress-tensor, which is assumed to be symmetrical, are denoted by t^{ij}. The vector $\boldsymbol{f}$ describes the (mass-specific) density of external momentum supply. Typical momentum supply terms are the gravitational acceleration or the Lorentz-force (per unit mass),

$$f^i = (Q\,\mathfrak{E}^i + \varepsilon_{ijk}\, I^j B^k)/\varrho\,, \tag{2.9}$$

with the permutation symbol ε_{ijk}, the volume charge-density

$$Q = \sum_{\alpha=1}^{\nu} \frac{q_\alpha}{m_\alpha} \varrho_\alpha , \tag{2.10}$$

the conductive flux-density

$$I^i = \sum_{\alpha=1}^{\nu} \frac{q_\alpha}{m_\alpha} \varrho_\alpha \, w^i{}_\alpha \tag{2.11}$$

and the electromotive intensity

$$\mathfrak{E}^i = E^i + \varepsilon_{ijk} \, v^j B^k . \tag{2.12}$$

The balance equation for the internal energy of the mixture reads

$$\varrho \, (\partial \varepsilon / \partial t + v^i \, \varepsilon_{,i}) + q^i{}_{,i} = t^{ij} \, v^i{}_{,j} + \varrho \, r \tag{2.13}$$

with the (nonconvective) heat flux q^i and the energetic supply density r. An example for r is Joule's heating term

$$\varrho \, r = I^i \, \mathfrak{E}_i . \tag{2.14}$$

2.2. *Surface Equations of Balance*

For surface partial mass-densities γ_α the general balance (2.3) yields

$$\partial \gamma_\alpha / \partial t - 2 K_{\mathrm{M}} \, u \, \gamma_\alpha + (\gamma_\alpha \, u^A{}_\alpha)_{;A} + [\varrho_\alpha (v^i{}_\alpha - u^i{}_\alpha)] \, n_i = \tau_{\alpha \mathrm{s}} , \tag{2.15}$$

where $u^i{}_\alpha$ are the cartesian components of the mass velocity of the surface constituent α and $\tau_{\alpha\mathrm{s}}$ is the surface density of mass production. Introduction of mixture quantities yields the mass conservation of the mixture

$$\begin{aligned} \partial \gamma / \partial t - 2 K_{\mathrm{M}} \, u \, \gamma + u^A \, \gamma_{,A} + \gamma \, u^A{}_{;A} & \\ = - [\varrho \, (v^i - u^i)] \, n_i & \end{aligned} \tag{2.16}$$

with

$$\gamma = \sum_{\alpha=1}^{\nu_{\mathrm{s}}} \gamma_\alpha , \quad \gamma \, u^i = \sum_{\alpha=1}^{\nu_{\mathrm{s}}} \gamma_\alpha \, u^i{}_\alpha , \quad w^i{}_{\alpha\mathrm{s}} = u^i{}_\alpha - u^i .$$

Analogously to (2.7), the surface mass production $\tau_{\alpha\mathrm{s}}$ can be calculated from stoichiometric coefficients $\gamma^a_{\alpha\mathrm{s}}$ and reaction rates Λ^a_{s}:

$$\tau_{\alpha\mathrm{s}} = \sum_{a=1}^{n_{\mathrm{s}}} \gamma^a_{\alpha\mathrm{s}} \, m_\alpha \, \Lambda^a_{\mathrm{s}} . \tag{2.17}$$

The surface momentum balance law is expressed in terms of space components as

$$\begin{aligned} \gamma \, (\partial u^i / \partial t + u^A \, u^i{}_{,A}) - t_{\mathrm{s}}{}^{iA}{}_{;A} + [\varrho \, (v^i - u^i)(v^j - u^j) - t^{ij}] \, n_j & \\ = \gamma \, f_{\mathrm{s}}^i . & \end{aligned} \tag{2.18}$$

Decomposition into tangential and normal components gives

$$\begin{aligned} \gamma \, (\partial u^D / \partial t + u^A \, u^D{}_{;A} - 2 u \, u^A \, \Omega^D{}_A - u \, u_{,A} \, h^{AD}) - t_{\mathrm{s}}{}^{AD}{}_{;A} & \\ = - [\varrho \, (v^D - u^D)(v^i - u^i) - t^{Di}] \, n_i + \gamma \, f_{\mathrm{s}}^{\mathrm{D}} , & \end{aligned} \tag{2.19}$$

$$\begin{aligned} \gamma \, (\partial u / \partial t + 2 u^A \, u_{,A} + u^A \, u^B \, \Omega_{AB}) - t_{\mathrm{s}}{}^{AB} \, \Omega_{AB} & \\ + [\varrho \, (v^n - u)^2 - t^{nn}] = \gamma \, f_{\mathrm{s}}^n . & \end{aligned}$$

Here $t_{\mathrm{s}}{}^{iA} = h^i_B t_{\mathrm{s}}{}^{AB}$ are the mixed components of the surface stress tensor $t_{\mathrm{s}}{}^{AB}$, while $f^i{}_{\mathrm{s}}$ is the surface momentum supply. With Ω_{AB} we denote the second fundamental form of the surface. An example for $f^i{}_{\mathrm{s}}$ is again the Lorentz-force term

$$f^i{}_{\mathrm{s}} = (Q_{\mathrm{s}} \langle \mathfrak{E}^i{}_{\mathrm{s}} \rangle + \varepsilon_{ijk} \, I^{j\mathrm{s}} \, \langle B^k \rangle) / \varrho \tag{2.20}$$

with the surface charge density,

$$Q_{\mathrm{s}} = \sum_{\alpha=1}^{\nu_{\mathrm{s}}} \frac{q_\alpha}{m_\alpha} \gamma_\alpha , \tag{2.21}$$

the surface conduction flux-density

$$I_{\mathrm{s}}{}^i = \sum_{\alpha=1}^{\nu} \frac{q_\alpha}{m_\alpha} \gamma_\alpha \, w_{\alpha\mathrm{s}}{}^i \tag{2.22}$$

and the electromotive intensity of the surface

$$\mathfrak{E}_{\mathrm{s}}{}^i = E^i + \varepsilon_{ijk} \, u^j \, B^k . \tag{2.23}$$

By $\langle F \rangle$ we denote the (arithmetical) mean

$$\langle F \rangle = (F^+ + F^-)/2 , \tag{2.24}$$

where F^+, F^- are the respective limits of F towards S from the adjacent volumina V^+ and V^-. The balance of the surface energetic ε_{s} has the form

$$\begin{aligned} \gamma \, (\partial \varepsilon_{\mathrm{s}} / \partial t + u^A \, \varepsilon_{\mathrm{s},A}) + q_{\mathrm{s}}{}^A{}_{;A} & \\ + [\varrho \, (\varepsilon - \varepsilon_{\mathrm{s}} + \tfrac{1}{2} (\boldsymbol{v} - \boldsymbol{u})^2)(v^i - u^i) + q^i] \, n_i & \\ = t_{\mathrm{s}}{}^{iA} \, u^i{}_{,A} + \gamma \, r_{\mathrm{s}} + [t^{ij} (v^j - u^j)] \, n_i . & \end{aligned} \tag{2.25}$$

With q_{s}^A we denote the surface heat flux and with γ_{s} the supply density of the surface energetic. Again an example for r_{s} is Joule's heating term

$$r_{\mathrm{s}} = I^i{}_{\mathrm{s}} \, \mathfrak{E}^i{}_{\mathrm{s}} / \gamma . \tag{2.26}$$

2.3. *Maxwell-Equations*

If electromagnetic fields play a rôle one has to consider the balance equations for the electrical charge and the magnetic flux as well, which in volumes V^+

or V^- without singular surfaces read

$$\begin{aligned} D^i{}_{,i} &= Q, \\ \varepsilon_{ijk} E^k{}_{,j} &= -B^i{}_{,t}, \\ B^i{}_{,i} &= 0, \\ \varepsilon_{ijk} H^k{}_{,j} &= Q v^i + I^i + D^i{}_{,t}, \end{aligned} \tag{2.27}$$

with the electric field E^i, the magnetic field H^i, the magnetic flux-density B^i and the electric displacement density D^i. In addition there are jump conditions at surfaces where electromagnetic fields are discontinuous. If one introduces only volume electromagnetic fields, these conditions are

$$\begin{aligned} [D^i]\, n_i &= Q_s, \\ \varepsilon_{ijk} n^j [E^k] &= u\, [B_i], \\ [B^i]\, n_i &= 0, \\ \varepsilon_{ijk} n^j [H^k] &= Q_s u^i + I^i{}_s - u\, [D^i]. \end{aligned} \tag{2.28}$$

2.4. *Comments on the Balance Equations*

Although the system of balance equation as presented here is far from being complete in the sense of field eqations, it should be worthwhile to add some remarks.

Relations Among the Charge Densities

There are two ways to obtain a balance for the volume charge density. One way proceeds via the balances for the partial mass densities to give

$$\begin{aligned} 0 &= \sum_{\alpha=1}^{\nu} \frac{q_\alpha}{m_\alpha} \left(\varrho_{\alpha,t} + (\varrho_\alpha v_\alpha{}^i)_{,i} - \sum_{a=1}^{n} \Lambda^a \gamma_\alpha{}^a m_\alpha \right) \\ &= Q_{,t} + (Q v^i + I^i)_{,i} - \sum_{\alpha, a=1}^{n,\nu} \Lambda^a \gamma_\alpha^a q_\alpha \end{aligned} \tag{2.29}$$

by summation weighted with q_α/m_α. The other way proceeds via certain differential operations on the Maxwell equations, $(2.27)_1$ and $(2.27)_4$, to give

$$\begin{aligned} 0 &= (Q - D^i{}_{,i})_{,t} + (Q v^i + I^i + D^i{}_{,t} - \varepsilon_{ijk} H^k{}_{,j})_{,i} \\ &= Q_{,t} + (Q v^i + I^i)_{,i}\,. \end{aligned} \tag{2.30}$$

Both equations are identical if one assumes charge conservation:

$$0 = \sum_{\alpha, a=1}^{\nu, n} \Lambda^a \gamma^a{}_\alpha q_\alpha\,. \tag{2.31}$$

Surprisingly, the same reasoning applies to the surface equations as well. Weighted summation on the partial surface mass balances gives

$$\begin{aligned} 0 = \sum_{\alpha=1}^{\nu_s} \frac{q_\alpha}{m_\alpha} \Bigg(& \gamma_{\alpha,t} - 2 K_M u \gamma_\alpha + (\gamma_\alpha u^A{}_\alpha)_{;A} \\ & + [\varrho_\alpha (v^i{}_\alpha - u^i{}_\alpha)]\, n_i - \sum_{a=1}^{n_s} \Lambda^a{}_s \gamma^a{}_{s\alpha} m_\alpha \Bigg) \\ = Q_{s,t} - 2 & K_M u Q_s + (Q_s u^A + I^A{}_s)_{;A} \\ & + [Q(v^i - u^i) + I^i]\, n_i - \sum_{\alpha, a=1}^{\nu_s, n_s} \Lambda^a{}_s \gamma^a{}_{s\alpha} q_\alpha\,. \end{aligned} \tag{2.32}$$

With help of compatibility conditions for derivatives of discontinuous fields as they are presented e.g. by Cohen and Wang [18] one may apply the same differential operations as above to the jump conditions $(2.28)_1$ and $(2.28)_4$. This yields

$$\begin{aligned} 0 &= (Q_s - [D^i]\, n_i)_{,t} + (Q_s v^i + I^i{}_s - [D^i]\, u - \varepsilon_{ijk} [H^k]\, n_j)_{,i} \\ &= Q_{s,t} - 2 K_M u Q_s + (Q_s u^A + I^A{}_s)_{;A} + [Q(v^i - u^i) + I^i]\, n_i\,. \end{aligned} \tag{2.33}$$

Again both equations become identical if charge is conserved,

$$0 = \sum_{\alpha, a=1}^{\nu_s, n_s} \Lambda^a{}_s \gamma^a{}_{s\alpha} q_\alpha\,. \tag{2.34}$$

So it is the concept of charge conservation that assures equations for charge densities deduced on seemingly independent ways to be nevertheless consistent with each other.

Electromagnetic Production Terms

Since the mechanical momentum of a fluid in an electromagnetic field is not conserved, the respective production term, which – by experience – is given by the Lorentz force, does not vanish. As to the surface production density one has to take into account that the electromagnetic fields may suffer a jump at the surface. So one has to use the arithmetical mean from values for the respective fields from both sides of the surface in order to calculate the Lorentz term. Concerning the surface production of internal energy there is a small difference. This is due to the fact that $(2.28)_2$ displays the continuity of the tangential components of the surface electromotive intensity across the surface, which in turn gives the Joule term by multiplication with the (surface inherent) electric conduction current. Therefore in the balance of the surface energetic the mean does not need to be applied.

Choice of Fields in Volumes and Surfaces

We assumed that electromagnetic fields need to be defined only in volumes. They have a discontinuity at some singular surface but no surface specific electromagnetic fields are introduced. As a consequence, the potential is continuous across the surface. For the characterization of surfaces with discontinuous potential (e.g. electric double layers) one has to extend the formalism to allow for surface specific electromagnetic fields with general dependence on surface coordinates and time. Despite this choice for nonsingular electromagnetic fields we assume the charge and current fields to become eventually singular at the surface, which is accounted for by the introduction of the respective surface specific fields.

Influence of the Moving Boundary on the Mass Velocity

Typical examples for moving boundary problems are the classical Stefan problem of a melting front or the surface modification by etching. The moving surface is a phase boundary of arbitrary shape on which a thin layer of material may be adsorbed (e.g. in dry etching). The mass density ratio solid state/fluid is rather large. For the moment we assume the adsorbed layer to be stationary; $\gamma_{,t} = 0$ and $u^A = 0$. In addition, we assume the solid to be at rest, i.e. $v^i = 0$. Then the surface mass balance gives

$$v_n^+ = \left(2\,\frac{K_\mathrm{M}\,\gamma}{\varrho^+} + 1 - \frac{\varrho^-}{\varrho^+}\right) u\,. \tag{2.35}$$

With vanishing boundary velocity u one restores the ordinary kinematical boundary condition of vanishing normal velocity. The dependence of v_n on u is linear. Because of the great mass density ratio the mass velocity v_n in general will have a reversed sign with respect to u. So a downward moving melting or etch front corresponds to an upward mass flow. It is concluded that the supply of reactants to the surface proceeds by mere downward diffusion and never by convection. However, this general behaviour may change in the vicinity of a point with large positive curvature K_M (convex surface), if we have a nonvanishing surface mass density, as is indicated by the first term in the brackets of (2.35).

Influence of the Moving Boundary on Surface Charges

There are situations where a moving boundary has to be considered together with surface charges, e.g. in plasma etching. It is interesting to discuss the surface balance of momentum under such circumstances. If in addition to the last paragraph we assume vanishing magnetic flux density the normal component of the surface momentum balance becomes

$$\begin{aligned}\gamma\, u_{,t} - t_\mathrm{s}{}^{AB}\,\Omega_{AB} + (4\,K_\mathrm{M}^2\,\gamma^2 \\ -(4\,K_\mathrm{M}\,\gamma + \varrho^+)\,\varrho^- + \varrho^{-2})\,u^2/\varrho^+ - [t^{nn}] \\ = Q_\mathrm{s}\,\langle E^n\rangle = [D^n\,E^n - \tfrac{1}{2}\,D^k\,E_k] = \tfrac{1}{2}\,\varepsilon_0\,[E^{n2}] \\ = Q_\mathrm{s}\,E^{n+} - \tfrac{1}{2}\,Q_\mathrm{s}^2/\varepsilon_0\,,\end{aligned} \tag{2.36}$$

where the last equations are valid in a reference system with $D^i = \varepsilon_0\,E^i$. One can read (2.36) as pressure balance. The first term contributes, if the surface displacement accelerates or decelerates. The next term describes the action of the surface tension in regions with non-vanishing curvature. (While a soap bubble contracts, a pressure is induced in the bubble's interior.) The third term is a unfamiliar one and describes the reaction of a surface induced by the acceleration of the volume mass flow which is connected with the moving boundary. The last term on the l.h.s. gives the jump of the (mechanical) pressure between the two adjacent media. Accordingly the r.h.s. in this picture gives the jump of the (electrical) pressure. For the particular choice of stationary process ($u_{,t} = 0$) in a plane surface ($\Omega_{AB} = 0$) where the mechanical normal tensions cancel ($[t_{nn}] = 0$), (2.36) gives a surface charge corresponding to the mass flow:

$$Q_\mathrm{s} = (4\,K_\mathrm{M}^2\,\gamma^2 - (4\,K_\mathrm{M}\,\gamma + \varrho^+)\,\varrho^- + \varrho^{-2})\,u^2/(\langle E^n\rangle\,\varrho^+)\,.$$

Under the same circumstances as above the tangential components of the surface momentum balance read

$$\begin{aligned}\gamma\,u\,u_{,A}\,h^{AD} - t_\mathrm{s}{}^{AD}{}_{;A} + \varrho^+\,v^{D+}\,(v^{n+} - u) - [t^{Dn}] \\ = Q_\mathrm{s}\,E^D = [D^n\,E^D]\,.\end{aligned} \tag{2.37}$$

In the picture of a pressure balance the first term in (2.37) gives the resulting drag or pressure from a lateral moving boundary. The second term corresponds to the usual pressure gradient. A shear stress from volume flow is contributed by the third term provided we have a nonvanishing slip velocity. The last term on the l.h.s. gives the jump of the volume shear stress tensor. The r.h.s. can be interpreted either by giving the usual electrical supply of lateral momentum or as jump of the electrical volume stress tensor.

3. Boundary Conditions

One important application of surface balances is to supply the volume field equations with boundary conditions.

This surface can either be given a priori (e.g. as the walls of a container) or may be calculated as part of the solution (e.g. with moving boundaries). In conventional volume problems (in V^+, see Fig. 4) one gives boundary values for the fields on the side ∂V^+ of S. However, if S is a two-dimensional material continuum in interaction with V^+ the boundary values at ∂V^+ are not known. Instead one has to give boundary conditions on the side ∂V^- of S. To determine the surface fields and the boundary values at V^+ it is necessary (although surely not sufficient!) that there are as many relations as unknowns. According to Table 1 we have to calculate $7\,v_s+n_s+51$ fields.

The most obvious equations at hand are v_s+4 equations of balance. The Maxwell jump conditions give 6 independent equations whereas the special choice (A.6) of the surface parameters adds 3 equations. Next we have v_s+10 boundary values at ∂V^-. This gives a total of $2\,v_s+23$ equations. As usual in continuum mechanics the missing equations are delivered by constitutive relations, by which the material response of the media is characterized. The first equations are the $2\,v_s+20$ volume constitutive equations of the media in V^+ and V^-. For the last $3\,v_s+8+n_s$ quantities which appear in the surface balances we introduce surface constitutive relations. Table 1 gives a provisional summary.

Table 1. Preliminary list of equations

v_s+4	Equations of balance for	$\gamma_\alpha, u^i, \theta$
6	Maxwell jump conditions for	E^{i+}, H^{i+}
3	Geometric conditions for	x^i
v_s+10	Boundary conditions at ∂V^- for	$\varrho_\alpha^-, v^{i-}, \vartheta^-, E^{i-}, H^{i-}$
v_s+10	Volume constitutive equations in V^- for	D^{i-}, B^{i-}, $t^{ni-}, \varepsilon^-, q^{n-}, w_\alpha{}^{n-}$
$3\,v_s+8+n_s$	Surface constitutive equations in S for	$\Lambda^a{}_s, t_s{}^{AB}, [t^{ni}], \varepsilon_s$ $[\varepsilon], q_s{}^A, [q^n], w_{\alpha s}{}^A, [w_\alpha{}^n]$
v_s+10	Volume constitutive equations in V^+ for	D^{i+}, B^{i+}, $t^{ni+}, \varepsilon^+, q^{n+}, w_\alpha{}^{n+}$
$7\,v_s+51+n_s$		

Table 2. Conclusive list of equations.

v_s+4	Equations of balance for	$\gamma_\alpha, u^i, \theta$
6	Maxwell jump conditions for	E^{i+}, H^{i+}
3	Geometric conditions for	x^i
v_s+16	Boundary conditions at ∂V^- for	$\varrho_\alpha^-, v^{i-}, \vartheta^-, E^{i-}, H^{i-}$, D^{i-}, B^{i-}
$4\,v_s+12+n_s$	Surface constitutive equations in S for	$\Lambda^a{}_s, t_s{}^{AB}, t^{ni\pm}, \varepsilon_s$, $\varepsilon^\pm, q_s{}^A, q^{n\pm}, w_{\alpha s}{}^A, w_\alpha{}^{n\pm}$
v_s+10	Volume constitutive equations in V^+ for	D^{i+}, B^{i+}, $t^{ni+}, \varepsilon^+, q^{n+}, w_\alpha{}^{n+}$
$7\,v_s+51+n_s$		

However, as mentioned above our surface S should serve as closure of V^+ against the rest of the world whereas the table tells us to develop a material theory in V^- in order to give the respective constitutive equations. This contradiction can be avoided if we eliminate volume constitutive equations in V^- by prescribing the respective quantities in other ways, e.g. as indicated by the arrows in Table.

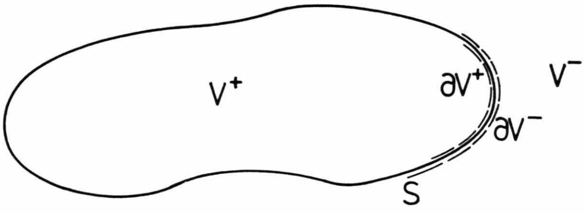

Fig. 4. Boundary conditions for field equations in V^+ can be given on two sides ($\partial V^+, \partial V^-$) of the bounding surface S.

Thus a necessary condition for the solution of a problem with a moving boundary in interaction with an enclosed volume is the establishment of all the equations listed in Table 2.

It seems that some points are worth mentioning:

- Contrary to the volume field equations there is no boundary value problem for the surface field equations as S is a closed surface.

- But this very closure of S may restrict the functional dependence of the fields on z^A (e.g. periodic dependence) such that the fields remain continuous or differentiable.

- The essential trick to complete the set of equations appears to be the use of volume constitutive equations in the vicinity of S. This closes the gap between the number of unknowns and the number of relations and is different in comparison with cases without surface fields.

- If there is additional knowledge about some quantities occurring, e.g. the vanishing of all γ_α, then accordingly the number of needed constitutive equations decreases. Even in the case of the vanishing of all surface quantities – when the surface balances reduce to the ordinary hydrodynamic jump conditions – there are surface constitutive equations for volume constitutive quantities, e.g. for $\langle q^n \rangle$ or $\langle t^{ni} \rangle$. It has been in connection with these latter relations that Waldmann [10] pointed out the possible use of the jump conditions in the discussion of boundary values.

- Concerning the practical application of the equations in Table 2 one has to discuss the region of validity for the description with jump terms. Jump terms describe discontinuities (in the direction of some surface normal) of fields on a macroscopic scale whereas on a microscopic scale the fields may be continuous (cf. Figure 2). In our model there are several scales to be considered. Jumps of the pressure tensor or of the temperature represent changes which are related to the scale of the mean free path. The relevant scale for the surface mass density (surface chemical and adsorption kinetics) is of the order of molecular diameters. If the electric field is related to a plasma, the appropriate scale for changes of the electric field is the Debye-length, whereas surface charges are related again to the scale of molecular diameters.

If all these different kinds of behaviour are lumped together into a description with jump terms, it is the largest scale which determines the "thickness" of the singular surface. Smaller structures are not resolvable. If one is just interested in these smaller structures the formalism is not applicable in the form presented. For a resolution of structures within the last mean free path in front of a wall, e.g., one has to do statistical mechanics. Then equations according to Table 3 are (still necessary but) not sufficient for the unique determination of a solution.

4. Constitutive Equations for Material Surfaces

In Table 2 some constitutive equations appear. They have been divided into volume constitutive equations (VCE) and surface constitutive equations (SCE). As to the VCEs, there are papers by Liu and Müller [19] as well as by Benach and Müller [20] which consider VCEs of fluids in electromagnetic fields. Therefore we will deal with SCEs in this article.

In the following we will be considered with SCE of fluids in electromagnetic fields. For the sake of simplicity in this first study on this subject we restrict ourselves to the case of the electrohydrodynamic approximation

$$E_i \gg \varepsilon_{ijk}\, v^j B^k .$$

This causes $\boldsymbol{B}$ to disappear and renders $\boldsymbol{E}$ to be an ordinary vector with respect to Galilean transformations. Fortunately, this specialization applies well to intended applications, e.g. low pressure plasma processing.

In the most general case one would assume the space and time dependent value of a certain constitutive quantity to depend on the history of all involved fields in the whole body. However, the resulting SCE are of functional type and thus by far too complex. In this situation we use some rules given by Truesdell and Toupin [21], which allow to reduce this generality.

According to the rule of equipresence, we assume that all response quantities depend on all fields, the surface fields as well as the fields of the adjacent volumina. The incorporation of volume fields to the list of arguments of SCE was motivated by work of Fisher and Leitman [15, 16], who showed in a simple example that the response function for q_n^+ needs the temperature in V^+ as well as that in V^- as arguments. Otherwise q_n^+ would vanish identically. In cases where the quality of the material memory is not good, one can approximate the history of a field in the sense of a Taylor expansion by a function of different time derivatives of the field. Analogously, if the action of a field is locally determined one can approximate the functional over the whole body by a function of several space derivatives of that field. The considered order of derivatives may be different for different fields.

In this sense we make a choice for the list of arguments to be used. By this choice we define a certain class of materials. It may happen that this class gives some approximation to the behaviour of some real material (this is of course hoped for with respect to application), but strictly this is not necessary. The pertaining arguments are

$$\gamma_\alpha, \gamma, u^i, \theta, \gamma_{\alpha,A}, \gamma_{,A}, \theta_{,A}, \varrho_\alpha{}^{\pm}, \varrho^{\pm}, \vartheta^{\pm}, v^{i\pm}, E^{i\pm}, h^i{}_A, h^i{}_{A;B} \tag{4.1}$$

(the two space-vectors $\boldsymbol{h}_A$ constitute the covariance surface base).

4.1. *Restriction by Conditions of Tensorial Invariance*

Following the rules of Truesdell and Toupin [21] we restrict the generality of the response functions by conditions of invariance. E.g., one would expect the material response to be independent of the motion of some observer. That leads to an invariance condition with respect to Galilean transformations. If the material exhibits isotropy in space, there are invariance conditions with respect to three-dimensional orthogonal transforms. In addition, we assume the material to exhibit isotropy in surface coordinates, which leads to invariancce conditions with respect to two-dimensional orthogonal transforms.

Fortunately we can exploit such implicit conditions by means of representation theorems which rest on the use of the Hamilton-Cayley-Theorem. A formidable list of representations has been given by Wang [22]. As result we give the preliminary form of the SCE of an isotropic fluid in an electric field as defined by (4.1).

$$
\begin{aligned}
s=s(&\gamma_\alpha, \gamma, \theta, \varrho_\alpha{}^{\pm}, \varrho^{\pm}, \vartheta^{\pm}, v^{\pm}{}_n-u, E^{\pm}{}_n, \Omega^A{}_A,\\
&\left[\begin{array}{@{}l@{\qquad}r@{}}
 & \gamma_{\alpha,A}\,\gamma_\beta{}^{,A}, \gamma_{\alpha,A}\,\gamma^{,A}, \gamma_{\alpha,A}\,\theta^{,A}, \gamma_{\alpha,A}(v^{\pm A}-u^A), \gamma_{\alpha,A}\,E^A,\\
 & \gamma_{,A}\,\gamma^{,A}, \gamma_{,A}\,\theta^{,A}, \gamma_{,A}(v^{\pm A}-u^A), \gamma_{,A}\,E^A,\\
 & \theta_{,A}\,\theta^{,A}, \theta_{,A}(v^{\pm A}-u^A), \theta_{,A}\,E^A,\\
 & (v^{\pm}{}_A-u_A)(v^{\pm A}-u^A), (v^{\pm}{}_A-u_A)\,E^A,\\
 & E_A\,E^A,\\
\text{2}^{\text{nd}}\text{ order} & \\
\Omega^{2A}{}_A, &
\end{array}\right.\\
&\left[\begin{array}{@{}l@{\qquad}r@{}}
 & \gamma_{\alpha,A}\,\Omega^{AB}\,\gamma_{\beta,B}, \gamma_{\alpha,A}\,\Omega^{AB}\,\gamma_{,B}, \gamma_{\alpha,A}\,\Omega^{AB}\,\theta_{,B}, \gamma_{\alpha,A}\,\Omega^{AB}(v^{\pm}{}_B-u_B), \gamma_{\alpha,A}\,\Omega^{AB}\,E_B,\\
 & \gamma_{,A}\,\Omega^{AB}\,\gamma_{,B}, \gamma_{,A}\,\Omega^{AB}\,\theta_{,B}, \gamma_{,A}\,\Omega^{AB}(v^{\pm}{}_B-u_B), \gamma_{,A}\,\Omega^{AB}\,E_B,\\
 & \theta_{,A}\,\Omega^{AB}\,\theta_{,B}, \theta_{,A}\,\Omega^{AB}(v^{\pm}{}_B-u_B), \theta_{,A}\,\Omega^{AB}\,E_B,\\
 & (v^{\pm}{}_A-u_A)\,\Omega^{AB}(v^{\pm}{}_B-u_B), (v^{\pm}{}_A-u_A)\,\Omega^{AB}\,E_B,\\
\text{3}^{\text{rd}}\text{ order} & E_A\,\Omega^{AB}\,E_B),
\end{array}\right.
\end{aligned}
\tag{4.2}
$$

$$
\begin{aligned}
v_A = {} & \sum_{\alpha=1}^{\nu_s-1} v_{1\alpha}\,\gamma_{\alpha,A}+v_2\,\gamma_{,A}+v_3\,\theta_{,A}+v_4(v^{+}{}_A-u_A)+v_5(v^{-}{}_A-u_A)+v_6\,E_A\\
&+\left(\sum_{\alpha=1}^{\nu_s-1} v_{7\alpha}\,\gamma_{\alpha,B}+v_8\,\gamma_{,B}+v_9\,\theta_{,B}+v_{10}(v^{+}{}_B-u_B)+v_{11}(v^{-}{}_B-u_B)+v_{12}\,E_B\right)\Omega^B{}_A,
\end{aligned}
\tag{4.3}
$$

$$
\begin{aligned}
t_{sAB} = {} & t_1\,h_{AB}+t_2\,\Omega_{AB}\\
&\left[\begin{array}{@{}l@{}}
+\sum\limits_{\alpha,\beta=1}^{\nu_s-1} t_{3\alpha\beta}\,\gamma_{\alpha,(A}\gamma_{\beta,B)}+\sum\limits_{\alpha=1}^{\nu_s-1} t_{4\alpha}\,\gamma_{\alpha,(A}\gamma_{,B)}+\sum\limits_{\alpha=1}^{\nu_s-1} t_{5\alpha}\,\gamma_{\alpha,(A}\theta_{,B)}\\
+\sum\limits_{\alpha=1}^{\nu_s-1} t_{6\alpha}\,\gamma_{\alpha,(A}(v^{+}{}_B-u_{B)})+\sum\limits_{\alpha=1}^{\nu_s-1} t_{7\alpha}\,\gamma_{\alpha,(A}(v^{-}{}_B-u_{B)})+\sum\limits_{\alpha=1}^{\nu_s-1} t_{8\alpha}\,\gamma_{\alpha,(A}E_{B)}
\end{array}\right.
\end{aligned}
$$

$$\begin{aligned}
&2^{\text{nd}}\ \text{order} \qquad\qquad (4.4)\\
&+t_9\,\gamma_{,(A}\gamma_{,B)}+t_{10}\,\gamma_{,(A}\theta_{,B)}+t_{11}\,\gamma_{,(A}(v^{+}{}_{B}-u_{B)})\\
&+t_{12}\,\gamma_{,(A}(v^{-}{}_{B}-u_{B)})+t_{13}\,\gamma_{,(A}E_{B)}+t_{14}\,\theta_{,(A}\theta_{,B)}+t_{15}\,\theta_{,(A}(v^{+}{}_{B}-u_{B)})\\
&+t_{16}\,\theta_{,(A}(v^{-}{}_{B}-u_{B)})+t_{17}\,\theta_{,(A}E_{B)}+t_{18}(v^{+}{}_{A}-u_{A})\,(v^{+}{}_{B}+u_{B})\\
&+t_{19}(v^{+}{}_{(A}-u_{A})\,(v^{-}{}_{B}-u_{B)})+t_{20}(v^{+}{}_{(A}-u_{A})\,E_{B)}\\
&+t_{21}(v^{-}{}_{A}-u_{A})\,(v^{-}{}_{B}-u_{B})+t_{22}(v^{-}{}_{(A}-u_{A})\,E_{B)}+t_{23}\,E_{A}\,E_{B}\\
&+\sum_{\alpha,\beta=1}^{\nu_s-1} t_{24\alpha\beta}\,\gamma_{,(A}\Omega_{B)}{}^{C}\gamma_{\beta,C}+\cdots+t_{59}\,E_{(A}\Omega_{B)}{}^{C}E_{C}\,.
\end{aligned}$$

In (4.2), s stands for the scalar valued constitutive quantities

$$\Lambda^{a}{}_{s},\ \varepsilon_{s},\ \varepsilon^{\pm},\ q_{n}{}^{\pm},\ w_{\alpha n}{}^{\pm},\ t_{nm}{}^{\pm}.$$

In (4.3) v_A stands for the vector valued constitutive quantities

$$t_{n}{}^{A\pm},\ q_{s}{}^{A},\ w_{s\alpha}^{\ A}\,.$$

The symbol $t_{s\,AB}$ denotes the surface stress tensor. The coefficients are all scalars in the sense of (4.2), and α, β run from 1 to ν_s-1. Round brackets denote symmetrization.

These expansions give the exact nonlinear representations of surface response functions and are by no means approximations in the sense of some expansion. For details of the calculation see [23]. This form of the SCEs is preliminary in the sense that for some response functions the list of arguments will be shortened by help of some entropy consideration, but it is conclusive with respect to the tensorial character of the SCE.

The importance of these results is best demonstrated by some examples. We have e.g. excluded the possibility that a scalar depends on arguments like $\theta_{,A}, \theta_{,A}\,\Omega^{AB}\,\Omega_{BC}\,E^{C}, \gamma_{\alpha,(A}\theta_{,B)}\,E^{(B}E^{C)}, \ldots$. Even more, vectorial SCEs depend in the most general case considered here, linearly on single components of vectorial arguments (e.g. $v_A(\Omega_{BC}, E_D) = \{v_6(\Omega^{B}{}_{B}, \Omega^{2B}{}_{B}, E^{B}E_{B}, E_{A}\Omega^{AB}E_{B})\,\delta_{A}{}^{C} + v_{12}(\Omega^{B}{}_{B}, \Omega^{2B}{}_{B}, E^{B}E_{B}, E_{A}\,\Omega^{AB}E_{B})\,\Omega_{A}{}^{C}\}\,E_{E}$). Nonetheless, these SCEs are of course nonlinear with respect to entire vectorial arguments via the coefficient functions. – In the case of a plain surface ($\Omega^{A}{}_{B}=0$), there is a further simplification: For scalars there are no arguments of 3rd order. For vectors only terms with $v_1, \ldots, v_6$ are important. For tensors only the first 23 terms have to be considered (e.g. $v_A(E_D) = v_6(E^{B}E_{B})\,E_{A}$).

4.2. *Restrictions by an Entropy Consideration*

It is a widely known fact that the second law of thermodynamics restricts the constitutive assumptions particularly in linear irreversible thermodynamics (compare e.g. de Groot and Mazur [24] or Meixner and Reik [11]). Rather than following their approach, we are looking for a method that allows for nonlinear SCE. For this aim we apply an entropy principle to the problem of SCE in a similar way as is common now in volume thermodynamics (cf. Müller [6] or Truesdell [25]).

We settle an entropy balance according to the general surface balance and assume the entropy surface density η_s and the entropy flux density Φ_s^A to be surface constitutive quantities like ε_s and q_s^A:

$$\begin{aligned}
&\gamma\left(\frac{\partial\eta_s}{\partial t}+u^{A}\,\eta_{s,A}\right)+\Phi_{s}{}^{A}{}_{;A}\\
&\qquad=-[\varrho\,(\eta-\eta_s)(v^{i}-u^{i})+\Phi^{i}]\,n_i+\gamma\,\sigma_s+\gamma\,s_s\,. \qquad (4.5)
\end{aligned}$$

Following Müller [26] we postulate for the entropy at some surface:

- The entropy supply should be a linear function of the supply of momentum and internal energy

$$s_s=\lambda_{si}\,f_{si}+\lambda_s\,r_s\,, \qquad (4.6)$$

λ_{si}, λ_s being handled as constitutive quantities.

- For all solutions of the surface field equations (= balance laws with introduced SCE) we assume

$$\sigma_s \geqq 0\,. \qquad (4.7)$$

Then we have to fulfill the inequality

$$\begin{aligned}
0\leqq\gamma&\left(\frac{\partial\eta_s}{\partial t}+u^{A}\,\eta_{s,A}\right)+\Phi_{s}{}^{A}{}_{;A}\\
&+[\varrho\,(\eta-\eta_s)(v^{i}-u^{i})+\Phi^{i}]\,n_i-\gamma\,s_s \qquad (4.8)
\end{aligned}$$

for all solutions of the field-equations.

The field-equations can be viewed as constraints that must be considered in the discussion of the inequality. There are several possibilities to exploit the inequality under these conditions (see Müller [6]). We proceed with a lemma of linear algebra proved by Liu [27]. This lemma states the equivalence of the following assertions:

(i) The inequality

$$A^{\sigma} X_{\sigma} + A \geqq 0 \tag{4.9}$$

is valid for all X_{σ} obeying the equations

$$A^{\mu\sigma} X_{\sigma} + B^{\mu} = 0 . \tag{4.10}$$

(ii) There are functions Λ_{μ} such that

$$A^{\sigma} - \Lambda_{\mu} A^{\mu\sigma} = 0 , \quad A - \Lambda_{\mu} B^{\mu} \geqq 0 \tag{4.11}$$

is valid.

For our application we identify the space and time derivatives of highest order of the fields (see line $1, \ldots, 4$ of Table 1) with the X_{σ}. The equations (4.10) then represent the abstract form of our field equations whereas (4.9) is the representation of the entropy inequality, $\mu = 1, \ldots, \nu_{\mathrm{s}} + 15$, $\sigma = 1, \ldots, 12\,\nu_{\mathrm{s}} + 66$, being generalized indices here.

The lemma makes use of the fact that in the balance laws as well as in the inequality, highest order derivatives occur linearly only. The introduced functions Λ_{μ} have the arguments of the response functions and u^i, v^i, $f_{i\mathrm{s}}$ and r_{s} as argument. With reference to the optimization calculus Liu named these functions "Lagrange"-multipliers.

The explicit form of

$$A^{\sigma} X_{\sigma} + A - \Lambda_{\mu} (A^{\mu\sigma} X_{\sigma} + B^{\mu}) \geqq 0 \tag{4.9a}$$

– the inequality with introduced constraints – is

$$\begin{aligned}
0 \leqq{} & \gamma \left(\frac{\partial \eta_{\mathrm{s}}}{\partial t} + u^A \eta_{\mathrm{s},A} \right) + \Phi_{\mathrm{s}}{}^{A}{}_{;A} \\
& \qquad + [\varrho (\eta - \eta_{\mathrm{s}})(v^i - u^i) + \Phi^i]\, n_i - \gamma (\lambda_{\mathrm{s}i} f_{\mathrm{s}}{}^i + \lambda_{\mathrm{s}} r_{\mathrm{s}}) \\
& - \Lambda_{\gamma} \left\{ \frac{\partial \gamma}{\partial t} - 2 K_{\mathrm{M}} u \gamma + \gamma u^A{}_{;A} + u^A \gamma_{,A} + [\varrho (v^i - u^i)]\, n_i \right\} \\
& - \sum_{\alpha=1}^{\nu-1} \Lambda_{\alpha} \left\{ \frac{\partial \gamma_{\alpha}}{\partial t} - 2 K_{\mathrm{M}} u \gamma_{\alpha} + \gamma_{\alpha} u^A{}_{;A} + u^A \gamma_{\alpha,A} + j_{\alpha\mathrm{s}}{}^{A}{}_{;A} \right. \\
& \qquad \left. + [\varrho_{\alpha} (v^i - u^i) + j_{\alpha}{}^i]\, n_i - \tau_{\alpha\mathrm{s}} \right\} \\
& - \Lambda_u{}^i \left\{ \gamma \left(\frac{\partial u^i}{\partial t} + u^A u^i{}_{,A} \right) - t_{\mathrm{s}}{}^{iA}{}_{;A} \right. \\
& \qquad \left. + [\varrho (v^i - u^i)(v^j - u^j) - t^{ij}]\, n_j - \gamma f_{\mathrm{s}}^i - Q_{\mathrm{s}} \langle E^i \rangle \right\} \\
& - \Lambda_{\varepsilon_{\mathrm{s}}} \left\{ \gamma \left(\frac{\partial \varepsilon_{\mathrm{s}}}{\partial t} + u^A \varepsilon_{\mathrm{s},A} \right) + q_{\mathrm{s}}{}^{A}{}_{;A} \right. \\
& \qquad + [\varrho (\varepsilon - \varepsilon_{\mathrm{s}} + \tfrac{1}{2} (\boldsymbol{v} - \boldsymbol{u})^2)(v^i - u^i) + q^i - t^{ij} (v^j - u^j)]\, n_i \\
& \qquad \left. - t_{\mathrm{s}}{}^{iA} u_{i,A} - I_{\mathrm{s}}{}^A E_A \right\} \\
& - \Lambda_{\Omega}{}^A \{ \varepsilon^{BC} \Omega_{AB;C} \} \\
& - \Lambda_h{}^{AB} \left\{ \frac{\partial h_{AB}}{\partial t} + 2 u \Omega_{AB} \right\} \\
& - \Lambda_{\Omega}{}^{AB} \left\{ \frac{\partial \Omega_{AB}}{\partial t} - u K_G h_{AB} + 2 K_{\mathrm{M}} u \Omega_{AB} - u_{,AB} \right\} \\
& - \Lambda_E{}^A \left\{ -[E_{n,A}] + \frac{1}{\varepsilon_0} \sum_{\alpha=1}^{\nu_{\mathrm{s}}-1} \left(\frac{q_{\alpha}}{m_{\alpha}} - \frac{q_{\nu}}{m_{\nu}} \right) \gamma_{\alpha,A} + \frac{q_{\nu}}{\varepsilon_0 m_{\nu}} \gamma_{,A} \right\} \\
& - \Lambda_E{}^3 \left\{ -[E_{n,t}] + \frac{1}{\varepsilon_0} \sum_{\alpha=1}^{\nu_{\mathrm{s}}-1} \left(\frac{q_{\alpha}}{m_{\alpha}} - \frac{q_{\nu}}{m_{\nu}} \right) \frac{\partial \gamma_{\alpha}}{\partial t} + \frac{q_{\nu}}{\varepsilon_0 m} \frac{\partial \gamma}{\partial t} \right\} .
\end{aligned} \tag{4.9b}$$

The notation for the Λ_{μ} is self-explanatory. This inequality is satisfied, if the conditions of part (ii) of the lemma are fulfilled. From $(4.11)_1$ we get the following result:

$$\mathrm{d}\eta_{\mathrm{s}} \overset{(1)}{=} \Lambda_{\varepsilon_{\mathrm{s}}} \mathrm{d}\varepsilon_{\mathrm{s}} - \frac{\Lambda_{\varepsilon_{\mathrm{s}}} \pi}{\gamma^2} \mathrm{d}\gamma - \frac{1}{\gamma^2} \sum_{\alpha=1}^{\nu_{\mathrm{s}}-1} \Lambda_{\alpha} (\gamma\, \mathrm{d}\gamma_{\alpha} - \gamma_{\alpha} \mathrm{d}\gamma), \quad \varepsilon_{\mathrm{s}} \overset{(2)}{=} \varepsilon_{\mathrm{s}}(\gamma_{\alpha}, \gamma, \theta), \quad \Lambda_{\varepsilon_{\mathrm{s}}} \overset{(3)}{=} \Lambda_{\varepsilon_{\mathrm{s}}}(\gamma_{\alpha}, \gamma, \theta),$$

$$\Lambda_{\gamma} \overset{(4)}{=} \gamma \left(\frac{\partial \eta_{\mathrm{s}}}{\partial \gamma} - \Lambda_{\varepsilon_{\mathrm{s}}} \frac{\partial \varepsilon_{\mathrm{s}}}{\partial \gamma} \right) = \Lambda_{\gamma}(\gamma_{\alpha}, \gamma, \theta), \quad \Lambda_{\alpha} \overset{(5)}{=} \gamma_{\alpha} \left(\frac{\partial \eta_{\mathrm{s}}}{\partial \gamma_{\alpha}} - \Lambda_{\varepsilon_{\mathrm{s}}} \frac{\partial \varepsilon_{\mathrm{s}}}{\partial \gamma_{\alpha}} \right) \overset{(6)}{=} \Lambda_{\alpha}(\gamma_{\alpha}, \gamma, \theta),$$

$$\Lambda_u{}^i \overset{(7)}{=} \Lambda_{\Omega}{}^A \overset{(8)}{=} \Lambda_{\Omega}{}^{AB} \overset{(9)}{=} \Lambda_h{}^{AB} \overset{(10)}{=} \Lambda_E{}^i \overset{(11)}{=} 0, \quad t_{\mathrm{s}}{}^{AB} \overset{(12)}{=} \frac{1}{\Lambda_{\varepsilon_{\mathrm{s}}}} \left(\gamma \Lambda_{\gamma} + \sum_{\alpha=1}^{\nu_{\mathrm{s}}-1} \gamma_{\alpha} \Lambda_{\alpha} \right) h^{AB} \overset{(13)}{=} -\pi h^{AB},$$

$$\begin{aligned}
&\Phi_{\mathrm{s}}{}^{A} \overset{(16)}{=} \Lambda_{\varepsilon_{\mathrm{s}}}\, q_{\mathrm{s}}{}^{A} + \sum_{\alpha=1}^{\nu_{\mathrm{s}}-1} \Lambda_{\alpha}\, j_{\alpha\mathrm{s}}{}^{A}, \quad \lambda_{i\mathrm{s}} \overset{(14)}{=} 0, \quad \lambda_{\mathrm{s}} \overset{(15)}{=} \Lambda_{\varepsilon_{\mathrm{s}}}, \\
&\Lambda_{a\mathrm{s}} \overset{(17)}{=} \Lambda_{a\mathrm{s}}(\ldots \text{ cf. } (4.2) \ldots), \quad \varepsilon^{\pm} \overset{(18)}{=} \varepsilon^{\pm}(\ldots \text{ cf. } (4.2) \ldots), \\
&q^{n\pm} \overset{(19)}{=} q^{n\pm}(\ldots \text{ cf. } (4.2), \quad w_{\alpha}{}^{n\pm} \overset{(20)}{=} w_{\alpha}{}^{n\pm}(\ldots \text{ cf. } (4.2) \ldots), \\
&t_{nA}{}^{\pm} \overset{(21)}{=} \sum_{\alpha=1}^{\nu_{\mathrm{s}}-1} t_{1\alpha}\, \gamma_{\alpha,A} + t_2\, \gamma_{,A} + t_3\, \theta_{,A} + t_4 (v_A{}^{+} - u_A) + t_5 (v_A{}^{-} - u_A) + t_6\, E_A \\
&\qquad + \left(\sum_{\alpha=1}^{\nu_{\mathrm{s}}-1} t_{7\alpha}\, \gamma_{\alpha,B} + t_8\, \gamma_{,B} + t_9\, \theta_{,B} + t_{10} (v_B{}^{+} - u_B) + t_{11} (v_B{}^{-} - u_B) + t_{12}\, E_B \right) \Omega^{B}{}_{A}, \\
&q_{\mathrm{s}A} \overset{(22)}{=} \sum_{\alpha=1}^{\nu_{\mathrm{s}}-1} q_{1\alpha}\gamma_{\alpha,A} + q_2\, \gamma_{,A} + q_3\, \theta_{,A} + q_4 (v_A{}^{+} - u_A) + q_5 (v_A{}^{-} - u_A) + q_6\, E_A \\
&\qquad + \left(\sum_{\alpha=1}^{\nu_{\mathrm{s}}-1} q_{7\alpha}\, \gamma_{\alpha,B} + q_8\, \gamma_{,B} + q_9\, \theta_{,B} + q_{10} (v_B{}^{+} - u_B) + q_{11} (v_B{}^{-} - u_B) + q_{12}\, E_B \right) \Omega^{B}{}_{A}, \\
&w_{\beta\mathrm{s}A} \overset{(23)}{=} \sum_{\alpha=1}^{\nu_{\mathrm{s}}-1} w_{1\beta\alpha}\, \gamma_{\alpha,A} + w_{2\beta}\, \gamma_{,A} + w_{3\beta}\, \theta_{,A} + w_{4\beta} (v_A{}^{+} - u_A) + w_{5\beta} (v_A{}^{-} - u_A) + w_{6\beta}\, E_A \\
&\qquad + \left(\sum_{\alpha=1}^{\nu_{\mathrm{s}}-1} w_{7\beta\alpha}\, \gamma_{\alpha,B} + w_{8\beta}\, \gamma_{,B} + w_{9\beta}\, \theta_{,B} + w_{10\beta} (v_B{}^{+} - u_B) + w_{11\beta} (v_B{}^{-} - u_B) + w_{12\beta}\, E_B \right) \Omega^{B}{}_{A},
\end{aligned} \tag{4.12}$$

and $(4.11)_2$ gives the remaining inequality $\left(\text{with } \phi^i = \Lambda_{\varepsilon}\, q^i + \sum_{\alpha=1}^{\nu} \Lambda_{\varrho_\alpha}\, j^i_{\alpha}\right)$

$$\begin{aligned}
0 \leqq &- \left\{ \frac{\partial \Lambda_{\varepsilon_{\mathrm{s}}}}{\partial \theta}\, q_{\mathrm{s}}{}^{A} + \sum_{\alpha=1}^{\nu-1} \frac{\partial \Lambda_{\alpha}}{\partial \theta}\, j_{\alpha\mathrm{s}}{}^{A} \right\} \theta_{,A} - \left\{ \frac{\partial \Lambda_{\varepsilon_{\mathrm{s}}}}{\partial \gamma}\, q_{\mathrm{s}}{}^{A} + \sum_{\alpha=1}^{\nu-1} \frac{\partial \Lambda_{\alpha}}{\partial \gamma}\, j_{\alpha\mathrm{s}}{}^{A} \right\} \gamma_{,A} \\
&- \sum_{\alpha=1}^{\nu-1} \left\{ \frac{\partial \Lambda_{\varepsilon_{\mathrm{s}}}}{\partial \gamma_{\alpha}}\, q_{\mathrm{s}}{}^{A} + \sum_{\beta=1}^{\nu-1} \frac{\partial \Lambda_{\beta}}{\partial \gamma_{\alpha}}\, j_{\beta\mathrm{s}}{}^{A} \right\} \gamma_{\alpha,A} + \Lambda_{\varepsilon_{\mathrm{s}}}\, I_{\mathrm{s}}{}^{A}\, E_A \\
&+ \sum_{\alpha=1}^{\nu-1} \Lambda_{\alpha} \tau_{\alpha\mathrm{s}} + \Bigg[\Bigg(\Bigg\{ \varrho \left\langle \eta - \eta_{\mathrm{s}} - \Lambda_{\varepsilon_{\mathrm{s}}} \left(\varepsilon - \varepsilon_{\mathrm{s}} + \tfrac{1}{2} (\boldsymbol{v} - \boldsymbol{u})^2\right) - \Lambda_{\gamma} \right\rangle - \sum_{\alpha=1}^{\nu-1} \gamma_{\alpha}\, \Lambda_{\alpha} \Bigg\} \delta^{ij} + \Lambda_{\varepsilon_{\mathrm{s}}}\, t^{ij} \Bigg) (v_j - u_j) \\
&\qquad + (\Lambda_{\varepsilon} - \Lambda_{\varepsilon_{\mathrm{s}}})\, q^i + \sum_{\alpha=1}^{\nu-1} (\Lambda_{\varrho\alpha} - \Lambda_{\alpha})\, j_{\alpha}{}^{i} \Bigg] n_i \\
&= \Sigma^{*}(\gamma_{\alpha}, \gamma, \theta, \gamma_{\alpha,A}, \gamma_{,A}, \theta_{,A}, \varrho_{\alpha}{}^{\pm}, \varrho^{\pm}, \vartheta^{\pm}, v^{i\pm}, E^{i\pm}) \qquad \text{for} \quad \alpha = 1, \ldots, \nu - 1, \\
&= \Sigma(\gamma_{\alpha}, \Lambda_{\mathrm{s}}{}^{a}, \gamma, \Lambda_{\varepsilon_{\mathrm{s}}}, j_{\beta\mathrm{s}}{}^{A}, \gamma_{,A}, q_A, j_{\beta}{}^{n\pm}, \varrho^{\pm}, \Lambda_{\varepsilon}{}^{\pm}, v^{i\pm}, E^{i\pm}) \quad \text{for } a = 1, \ldots, n_{\mathrm{s}},\ \alpha = n_{\mathrm{s}} + 1, \ldots, \nu - 1,\ \beta = 1, \ldots, \nu - 1.
\end{aligned} \tag{4.13}$$

The derived restrictions are valid for any material of the class defined by (4.1). On this level of generality we cannot derive any more constraints. This would only be possible under more specialized conditions, e.g. in thermodynamic equilibrium. However, if one is interested in special SCEs for a specific fluid one has to do kinetic theory calculations or experiments concerning the coefficient functions of the response functions.

4.3. Equilibrium

With thermodynamic equilibrium we denote a state of the process with vanishing entropy production, i.e. in (4.13) the sign of equality holds. We will discuss equilibrium for two cases identifying the r.h.s. of (4.13) with the indicated function Σ.

(i) Impermeable Membrane

If the material of the surface S is strictly impermeable for the fluids of the adjacent volumes we have

$$v^{n+} = u = v^{n-}, \quad j_\alpha{}^{n+} = 0 = j_\alpha{}^{n-}. \tag{4.14}$$

Obviously, for

$$q_{sA} \overset{(1)}{=} 0, \quad j_{s\alpha A} \overset{(2)}{=} 0, \quad \Lambda_{sa} \overset{(3)}{=} 0, \quad v^{A+} \overset{(4)}{=} u^A \overset{(5)}{=} v^{A-}$$

and

$$\Lambda_\varepsilon{}^+ \overset{(6)}{=} \Lambda_{\varepsilon_s} \overset{(7)}{=} \Lambda_\varepsilon{}^- \tag{4.15}$$

the function Σ attains its minimum, zero, thus fulfilling at least the necessary conditions for extrema

$$\begin{aligned}
&0 = \Lambda_{\varepsilon_s, A}\,, \\
&\Lambda_{\alpha, A} + \Lambda_{\varepsilon_s}\left(\frac{q_\alpha}{m_\alpha} - \frac{q_\nu}{m_\nu}\right) E_A = 0\,, \\
&\sum_{\alpha=1}^{\nu-1} \Lambda_\alpha\, \gamma^a_{\alpha s}\, m_\alpha = 0\,, \\
&t^{An\pm} = 0 = t^{An-}, \\
&q^{n+} = 0 = q^{n-}.
\end{aligned} \tag{4.16}$$

(ii) Semipermeable membrane

Let the material of S be permeable only for the constituent δ from the adjacent fluids. Then we have $v_\alpha{}^{n\pm} = u \ \forall \alpha \neq \delta$ and therefore

$$j_\beta{}^{n\pm} = \varrho_\beta\left(\frac{\varrho}{\varrho_\delta}\,\delta_{\beta\delta} - 1\right)(v^{n\pm} - u), \quad \forall \beta. \tag{4.17}$$

With that term the square brackets in the inequality (4.13) read

$$\begin{aligned}
0 \leqq \ldots + \Bigg[\Bigg(\Bigg\{&\varrho\,\langle \eta - \eta_s - \Lambda_{\varepsilon_s}(\varepsilon - \varepsilon_s + \tfrac{1}{2}(\boldsymbol{v} - \boldsymbol{u})^2) - \Lambda_\gamma \rangle \\
&- \sum_{\alpha=1}^{\nu-1} \varrho_\alpha \left(\Lambda_\alpha - (\Lambda_{\varrho\alpha} - \Lambda_\alpha)\left(\frac{1}{\varrho_\delta}\,\delta_{\alpha\delta} - \frac{1}{\varrho}\right)\varrho\right)\Bigg\}\,\delta^{ij} + \Lambda_{\varepsilon_s}\, t^{ij}\Bigg) \\
&\cdot (v_j - u_j) + (\Lambda_\varepsilon - \Lambda_{\varepsilon_s})\, q^i\Bigg]\, n_i \\
= \cdots + \Bigg[\Bigg(\Bigg\{&\varrho\,\Bigg\langle \eta - \Lambda_{\varepsilon_s}(\varepsilon + \tfrac{1}{2}(\boldsymbol{v} - \boldsymbol{u})^2) - \Lambda_{\varepsilon_s}\frac{1}{\varrho}\, t^{nn} \\
&+ \sum_{\alpha=1}^{\nu-1} \varrho_\alpha\, \Lambda_{\varrho\alpha}\left(\frac{1}{\varrho_\delta}\,\delta_{\alpha\delta} - \frac{1}{\varrho}\right)\Bigg\rangle \\
&- \varrho\,\langle \eta_s - \Lambda_{\varepsilon_s}\,\varepsilon_s + \Lambda_\gamma + \Lambda_\delta \rangle\Bigg\}\Bigg)(v^n - u) \\
&+ \Lambda_{\varepsilon_s}\, t^{nA}(v^A - u^A) + (\Lambda_\varepsilon - \Lambda_{\varepsilon_s})\, q^n\Bigg].
\end{aligned} \tag{4.18}$$

Dividing the appearing terms in surface specific ones and others we get with the introduction of

$$\begin{aligned}
\mu_\delta{}^\pm &= \varepsilon^\pm + \tfrac{1}{2}(\boldsymbol{v}^\pm - \boldsymbol{u})^2 + \frac{1}{\varrho}\, p^\pm \\
&\quad - \frac{1}{\Lambda_{\varepsilon_s}}\left\{\eta^\pm + \sum_{\alpha=1}^{\nu-1} \Lambda_{\varrho\alpha}{}^\pm \left(\delta_{\alpha\delta} - \frac{\varrho_\alpha{}^\pm}{\varrho^\pm}\right)\right\} \\
\mu_\delta{}^s &= \varepsilon^s + \frac{1}{\gamma}\,\pi - \frac{1}{\Lambda_{\varepsilon_s}}\left\{\eta^s + \sum_{\alpha=1}^{\nu-1} \Lambda_\alpha\left(\delta_{\alpha\delta} - \frac{\gamma_\alpha}{\gamma}\right)\right\}
\end{aligned} \tag{4.19}$$

the form

$$\begin{aligned}
0 \leqq \ldots &- [\varrho\,\Lambda_{\varepsilon_s}(\mu_\delta - \mu_\delta{}^s)(v^n - u)] \\
&+ \Lambda_{\varepsilon_s}[t^{nA}(v_A - u_A)] + [(\Lambda_\varepsilon - \Lambda_{\varepsilon_s})\, q^n]\,.
\end{aligned} \tag{4.20}$$

In addition to the equilibrium conditions from (4.15) we need $v^{n+} = u = v^{n-}$, and the corresponding necessary extremum conditions read

$$\mu_\delta{}^+ = \mu_\delta{}^s = \mu_\delta{}^-. \tag{4.21}$$

Obviously the jump of the quantities (4.19) vanishes in equilibrium at a semipermeable membrane. This is the motivation to identify the $\mu_\delta{}^\pm$, $\mu_\delta{}^s$ in equilibrium with the respective chemical potentials of constituent δ.

4.4. Further Consequences in Equilibrium

There are further conditions in equilibrium:

- From (4.19) we obtain

$$\Lambda_\delta = \Lambda_{\varepsilon_s}(\mu_\nu{}^s - \mu_\delta{}^s)\,. \tag{4.23}$$

Together with a Legendre transform from γ_α, γ, θ to $c_{\alpha s}$, γ, θ with $\gamma_\alpha = \gamma\, c_{\alpha s}$, (4.23) reveals $(4.12)_1$ as Gibbs' equation for a surface

$$\mathrm{d}\eta_s = \Lambda_{\varepsilon_s}\,\mathrm{d}\varepsilon_s - \frac{\Lambda_{\varepsilon_s}\,\pi}{\gamma^2}\,\mathrm{d}\gamma - \Lambda_{\varepsilon_s} \sum_{\alpha=1}^{\nu_s} \mu_s{}^\alpha\,\mathrm{d}c_{\alpha s}\,, \tag{4.24}$$

and the Lagrange-multiplier Λ_δ as representative for the chemical potential.

- Introduction of the equilibrium conditions in the vector SCE yields further restrictions for the coefficient functions in equilibrium:

$$\begin{aligned}
0 &= \sum_{\alpha=1}^{\nu-1} q_{1\alpha}\,\gamma_{\alpha, A} + q_2\,\gamma_{, A} + q_6\, E_A\,, \\
0 &= \sum_{\alpha=1}^{\nu-1} j_{1\alpha\beta}\,\gamma_{\beta, A} + j_{2\alpha}\,\gamma_{, A} + j_{6\alpha}\, E_A\,, \\
0 &= \sum_{\alpha=1}^{\nu-1} t^\pm{}_{1\alpha}\,\gamma_{\alpha, A} + t^\pm{}_2\,\gamma_{, A} + t^\pm{}_6\, E_A\,.
\end{aligned} \tag{4.25}$$

5. Discussion

5.1. The General Form of SCE

In (4.12) we presented the general results in a condensed form. In $(4.12)_1$ the total differential $d\eta_s$ is shown. According to $(4.12)_{2-6}$ η_s is a function of $\gamma_\alpha, \gamma, \theta$. Now, by $(4.15)_{6,7}$ one can show that in equilibrium Λ_{ε_s} becomes a function of θ alone. (From some volume entropy principle one has $\Lambda_\varepsilon^\pm = \Lambda_\varepsilon^\pm(\varrho_\alpha^\pm, \varrho^\pm, \vartheta^\pm)$, thus the independence of arguments in $(4.15)_{6,7}$ leads to contradictions unless one assumes $\Lambda_{\varepsilon_s} = \Lambda_{\varepsilon_s}(\theta)$.) This fact, together with the form of $(4.12)_1$ or (4.24) being that of a Gibbs' equation, motivates us to identify the integrating factor of the energetic in equilibrium with the inverse absolute temperature $\Lambda_{\varepsilon_s}(\theta) = 1/T(\theta)$. This is the reason for calling η_s entropy density while strictly speaking one should describe η_s as some function which exhibits the properties of entropy in the equilibrium (4.15).

Equation $(4.12)_7$ expresses the vanishing of the Lagrange-multiplier of the momentum balance, i.e. the momentum balance imposes no additional restrictions on the manifold of possible field functions. This happens to occur also in volume entropy principles and is related to the point of view that one can choose arbitrary fields $\gamma_\alpha, \gamma, u^i, x^i$, introduce them in the momentum field equation and calculate then the momentum supply f^i which just belongs to this choice of fields.

The equations $(4.12)_{8-10}$ express the vanishing of the geometrical "Lagrange"-multipliers. Obviously there are eight independent multipliers although we have only three geometric conditions (A.6). The reason is that we have replaced (A.6) by a system of geometric differential equations which (i) are linear in their highest derivatives and (ii) are – according to Truesdell and Toupin [21] – equivalent to (A.6). These relations also do not give restrictions in this context.

The same is true with reference to $(4.12)_{11}$, which yields the vanishing of the electromagnetic Lagrange-multiplier. Thus Maxwell's jump conditions do not give any restrictions, analogous to volume problems, cf. Müller [6].

Comparison of $(4.12)_{12,13}$ with (4.4) yields another example of simplifications due to the entropy consideration. For the considered class of materials, the stress tensor bears only the scalar surface tension π, which is similar to the hydrostatic pressure in volume problems. We conclude that such a fluid cannot suffer any shear stress. First, we do not have velocity gradients as arguments, thus viscous shear stress cannot be described. Secondly $t_s{}^{AB}$ is the mechanical stress tensor and does not describe electrical shear stress. Shear stress due to temperature gradients is only expected if the surface tension depends on $\theta_{,t}$, as one can see by comparison with VCEs for simple heat-conducting fluids.

The next equation, $(4.12)_{16}$, displays a linear dependence between the entropy flux and the dissipative phenomena of heat flux and diffusion flux as result. Nonetheless $(4.12)_{16}$ is a nonlinear relation between the flux of surface entropy and the field quantities. Since Λ_{ε_s} corresponds to $1/T_s$ in linear theories, the relation resembles to similar ones (derived by the assumption of Gibb's equation) in linear thermodynamics (cf. de Groot and Mazur [24]). But strictly speaking it differs from this, as Λ_{ε_s} and $\mu_{\alpha s}$ can be identified with inverse absolute temperature and with chemical potential, respectively, only in equilibrium whereas in nonequilibrium they are simply some SCE among others.

Equation $(4.12)_{16}$ displays the last restriction imposed on the SCE by the entropy principle in comparison with (4.2)–(4.4). The remaining response functions turn out to be unrestricted by the entropy principle. This is especially true for all SCE of volume constitutive quantities. – In the following we will illustrate these SCE by some examples. Generalizations to more general SCE turn out to be obvious.

The surface reaction rate is given by $(4.12)_{17}$. A classical relation is, e.g.

$$\Lambda_{1s} = k_1 \, e^{-E_1/kT} \gamma_1 \gamma_2 \tag{5.1}$$

for some surface reaction of second order, viz.

$$\gamma^1{}_1 A_1 + \gamma^1{}_2 A_2 \rightarrow \gamma^1{}_3 A_3 .$$

This is a typical nonlinear SCE. Other dependencies of Λ_s^a, e.g. on $\varrho_\alpha^\pm$ or $\boldsymbol{E}^\pm$ are conceivable, too.

Equations $(4.12)_{18-21}$ provide SCE for each single volume quantity, e.g. for $q_n{}^+$ and for $q_n{}^-$. Equivalently one may obtain equations for $[q_n]$ and for $\langle q_n \rangle$, as is often done in linear surface thermodynamics (cf. Bedeaux, Albano, and Mazur [12], Wolff and Albano [14] or Waldmann [10]). A possible example in relation to q_n is

$$\langle q_n \rangle = q_1 (\Lambda_\varepsilon^+ - \Lambda_\varepsilon^s) + (\Lambda_\varepsilon^- - \Lambda_\varepsilon^s) \, q_2 , \tag{5.2}$$

which gives a typical boundary relation for temperature jumps. The same reasoning applies to $(4.12)_{21}$, which is a vector SCE for the volume shear stress tensors. A classical representative is the slip flow condition (with the slip coefficients t_4, t_5)

$$\begin{aligned}\langle t_n{}^A\rangle &= t_4(v^{A+}-u^A)+t_5(v^{A-}-u^A)\\ &=\tfrac{1}{2}(t_4-t_5)(v^{A+}-v^{A-})\\ &\quad-\tfrac{1}{2}(t_4+t_5)(2u^A-(v^{A+}+v^{A-}))\,. \qquad (5.3)\end{aligned}$$

(Besides, conditions like (5.2), (5.3) for the means are also appropriate if the corresponding jumps can be calculated directly from the surface balances because of missing surface specific quantities.)

The physical significance of $(4.12)_{20}$ lies in the description of processes like adsorption. The most prominent example is adsorption according to Langmuir's adsorption-isotherm

$$\varrho_\alpha\, w^+_{\alpha n} = a^+_\alpha\, p^+_\alpha\left(1-\frac{1}{N_{\mathrm{ad}}}\sum_{\beta=1}^{\nu_s}\frac{\gamma_\beta}{m_\beta}\right)-b^+_\alpha\,\gamma_\alpha\,. \qquad (5.4)$$

Often in adsorption kinetics more complicated and nonlinear laws are known from experiments (cf. the BET-isotherm for multilayer adsorption, see Adamson [5]). In (5.4), a^+_α and b^+_α are phenomenological coefficients describing the surface-fluid interaction whereas N_{ad} is a measure of the number of adsorption sites.

Examples for the coefficients in $(4.12)_{22}$ are the surface heat conduction coefficient q_3 or the coefficient q_1 for the surface diffusion-thermo-effect. More cross-effects can be seen directly from the equation. All these effects can be nonlinear, as e.g. q_3 may be a function of $\theta^{,A}\,\theta_{,A}$ etc.

As to $(4.12)_{23}$, $w_{1\alpha\beta}$ is a lateral diffusion coefficient, $w_{3\alpha}$ gives a surface thermal-diffusion, and so on. Further interesting effects can be discussed in connection with the following linear combination:

$$\begin{aligned}I_{sA} &= \sum_{\alpha=1}^{\nu_s}\frac{q_\alpha}{m_\alpha}\, j_{\alpha sA}\\ &= \sum_{\alpha=1}^{\nu_s-1} j_{1\alpha}\,\gamma_{\alpha,A}+j_2\,\gamma_{,A}+j_3\,\theta_{,A}+j_4(v_A{}^+-u_A)\\ &\qquad\qquad +j_5(v_A{}^- -u_A)+j_6\,E_A\\ &\quad+\Bigg(\sum_{\alpha=1}^{\nu_s-1} j_{7\alpha}\,\gamma_{\alpha,B}+j_8\,\gamma_{,B}+j_9\,\theta_{,B}+j_{10}(v_B{}^+-u_B)\\ &\qquad\qquad +j_{11}(v_B{}^- -u_B)+j_{12}\,E_B\Bigg)\,\Omega^B{}_A\,, \qquad (5.5)\end{aligned}$$

which turns out to be identical with the lateral conduction current. With $j_6\,\delta^B{}_A+j_{12}\,\Omega^B{}_A$ we have obviously the electrical conductivity, which exhibits explicit tensorial behaviour due to the second fundamental form, the curvature tensor. Additionally an implicit geometric dependence is possible via the argument K_{M} for j_6 and j_{12}. Due to the arguments of j_6 and j_{12} the conductivity may depend on the surface temperature, on the electric field via $E^A E_A$, on the volume temperatures, on gradients of surface mass densities or temperature or even on the influence of (frictional) slip of the volume flow. According to the representation of a scalar SCE, interactions up to third order between these cross-effects are possible. – The term $j_3\,\delta^B{}_A+j_9\,\Omega^B{}_A$ is the coefficient for the thermo-current whereas $j_{4/5}\,\delta^B{}_A+j_{10/11}\,\Omega^B{}_A$ represent the coefficients for the electrophoretic current, i.e. a current induced by slip flow of the adjacent fluid relative to the surface. – In the case of a poorly conducting surface layer, e.g. a chemically adsorbed layer, we have $I_{sA}\approx 0$. Solving for E_A then gives

$$\begin{aligned}E_C = -(j_6\,\boldsymbol{\delta}+j_{12}\,\boldsymbol{\Omega})^{-1A}{}_C\Bigg[&\sum_{\alpha=1}^{\nu_s-1}(j_{1\alpha}\,\delta^B{}_A+j_{7\alpha}\,\Omega^B{}_A)\,\gamma_{\alpha,B}\\ &+(j_2\,\delta^B{}_A+j_6\,\Omega^B{}_A)\,\gamma_{,B}+(j_3\,\delta^B{}_A+j_9\,\Omega^B{}_A)\,\theta_{,B}\\ &+(j_4\,\delta^B{}_A+j_{10}\,\Omega^B{}_A)(v_B{}^+-u_B)\\ &+(j_5\,\delta^B{}_A+j_{11}\,\Omega^B{}_A)(v_B{}^- -u_B)\Bigg]\,. \qquad (5.6)\end{aligned}$$

From (5.6) one infers that a, say, lateral temperature gradient leads to an electric field which gives rise to the thermo-potential as well as slip velocities lead to an electric field which gives rise to the streaming-potential. (Streaming-potentials can cause strong hazards in aircraft-jets because of streaming fuel, see Adamson [5]). If with respect to the experimental setup solving (5.6) for, say, the relative velocity v_A-u_A is appropriate, effects as electrophoresis or thermophoresis can be described. If the slip is hindered we may get some osmotic pressure due to gradients in (surface) mass density, temperature or potential.

As a last comment on the SCE we give a hint to some peculiarities of the SCE in comparison to classical VCE.

- For SCE there are function arguments also from the outside of S (quasi-nonlocality due to the two different sides of S).
- There are SCE for volume constitutive quantities.
- SCE for volume response functions in V^+ have arguments from volume fields in V^- and vice versa.
- In the nonlinear case there are terms which describe interactions between either sides of the surface, e.g.

$$(v^{+A}-u^A)\,(v^-_A-u_A)\,,$$

or between one side and the surface itself, e.g.

$$(v^{+A}-u^{A})\,\theta_{,A}\,.$$

5.2. The Equilibrium Results

The equilibrium results are displayed by (4.15), (4.16), (4.21). The equations $(4.15)_{1,2}$ express the fact that the heat flux and the diffusion fluxes vanish. According to $(4.15)_3$ the rate of chemical reactions becomes zero. There is no further slip between the surface and the volume motion on either side (see $(4.15)_4$). It should be mentioned once more that $(4.15)_{6,7}$ expresses the equality between surface and volume temperatures. These conditions are taken as properties defining equilibrium. They lead to the results (4.16). With the equilibrium interpretation of Λ_{ε_s} as reciprocal absolute surface temperature, $(4.16)_1$ expresses the lateral homogeneity of the surface temperature. With $(4.16)_1$, $(4.16)_2$ indicates the vanishing of lateral gradients of the surface electrochemical potential whereas $(4.16)_3$ is the law of mass action. The classical form of the law of mass action is restored by introduction of the chemical potentials of ideal gases in the appropriate form into $(4.16)_3$. The last two results (4.16) describe the vanishing of the volume shear stress and of the volume normal heat flux on either side of the surface in equilibrium. (4.21) has already been discussed.

All these results, as consequences of the entropy argument, are thus results and not assumptions. That they can be derived from surface specific equations indicates that the notion of equilibrium takes over from the 3D-case to the 2D-case when properly adjusted.

5.3. Further Remarks

With the results established, another form of the entropy production can be derived:

$$\begin{aligned}\sigma_s = {} & \Lambda_{\varepsilon_s}(t_s{}^{AB}+\pi h^{AB})\,u_{A;B}+\Lambda_{\varepsilon_s} I_s{}^{A} E_A+\Lambda_{\varepsilon_s,A}\, q_s{}^{A}\\ & -\sum_{\alpha=1}^{\nu_s}(\Lambda_{\varepsilon_s}\mu_{\alpha s})_{,A}\, j_{\alpha s}{}^{A}-\Lambda_{\varepsilon_s}\sum_{\alpha=1}^{\nu_s}\mu_{\alpha s}\,\tau_{\alpha s}\\ & -[\varrho\,\Lambda_{\varepsilon_s}(\mu_\delta-\mu_{\delta s})(v^n-u)]+\Lambda_{\varepsilon_s}[t^{nA}(v_A-u_A)]\\ & +[(\Lambda_\varepsilon-\Lambda_{\varepsilon_s})\,q^n]\,. \end{aligned} \tag{5.8}$$

The first term on the r.h.s. of (5.8) vanishes in our case but would give some contribution if one considers nonzero surface viscosity. The second term arises from Joule's heat. The next two terms describe the dissipation due to heat resp. diffusion-fluxes. The last term in front of the square brackets accounts for the entropy production from chemical reactions. All these terms are analogous to corresponding volume expressions. The terms inside the square brackets yield particular surface contributions. The first one describes the entropy production due to the normal diffusion through the surface caused by a jump of the chemical potentials. The second bracket term contributes if slip leads to dissipation in connection with the off-diagonal elements of the volume stress tensor (e.g. because of viscosity). The last term contributes if a normal heat flux exists together with temperature jumps.

Together with the other results, these are similar – after appropriate simplification – to those from Wolff and Albano [14], Albano and Bedeaux [28] or Vodák [13]. Our form of the entropy production (5.8) is similar to that from the mentioned papers which, however, there appears as assumption and not as result as in the present paper. For the derivation of our SCE we nowhere use the assumption of local thermodynamic equilibrium. With respect to results from linear irreversible thermodynamics our results are slightly more general, as (i) we give a list of possible arguments for transport coefficients to account for scalar nonlinearities and (ii) in addition we present tensorial nonlinearities which go beyond the Curie-principle. Our work is also a generalization of the work of Moeckel [17] and Grauel [29] because of the consideration of electromagnetic fields, of any number of constituents and of chemical reactions.

The fact that there are no jump terms in our form of the Gibbs-Duhem-relation – which is contrary to Vodáks assumption – stems from the description of the surface as single, open, thermodynamic system. A generalization would consist in treating a small volume element which contains a part of S as well as parts of V^+ and V^-. Then the non-negativity of the entropy-production of a surface with respect to the volume-surface-interaction is described by

$$\sigma_+ + \sigma_s + \sigma_- \geqq 0\,. \tag{5.9}$$

(The production-densities are mass-specific!) Such a generalization is desirable because it yields restrictions for the SCE of volume fields, too, which is physically reasonable.

This form of the entropy principle would also be useful if the resulting restrictions turn out to be too strong (e.g. if the missing of shear-stress in nonequilibrium for the discussed material turns out to be non-physical). The change from (4.7) to (5.8) has a parallel in the theory of mixtures, where the non-negativity of the entropy production of the single constituents yielded too strong restrictions. so that only the condition of non-negative mixture entropy production could be imposed (cf. Bowen [7]).

6. Conclusion

In this paper we present a formalism establishing nonlinear constitutive functions for some material in interaction with a moving boundary in an electric field. The possible nonlinearity is important, as in particular in the vicinity of boundaries we are far from some equilibrium state. Besides the methodological questions the presentation has practical importance, too, as it yields the possibility of a consistent physico-geometrical description of problems with moving boundaries. For materials which are expected to behave differently the formalism can be applied to restrict response functions with another set of arguments.

Acknowledgement

I thank Prof. Dr. E. Richter, Braunschweig, for his kind support and many discussions. Thanks go also to the Division Fine Line Patterning of the Siemens AG, Munich, for financial and organisational support and to Dr. W. E. Köhler from the Technical Physics Division of Siemens AG, Erlangen, for valuable discussions.

Appendix: Geometric and Kinematic Relations

There are several possibilities to describe general curvilinear two-dimensional surfaces embedded in there-dimensional space (see e.g. Truesdell and Toupin [21]). One possibility is to define the locus of the surface implicitly by a function

$$f(\boldsymbol{x}, t) = 0, \qquad \text{(A.1)}$$

$\boldsymbol{x} = x^i \boldsymbol{e}_i$ being a position in cartesian coordinates x^i in the canonical basis $\boldsymbol{e}_i$ and t being the time. (Small, Latin indices denote three-dimensional, cartesian coordinates while capital Latin indices denote two-dimensional, curvilinear coordinates. Einstein's summation convention is used.) Under certain instances, the function f may be non-unique. An example for this to happen may be the description of a bubble in water. So for a general characterization the introduction of surface parameters z^A seems more convenient. The surface S_t in question is then localized via the embedding

$$\boldsymbol{x} = \boldsymbol{x}(z^A, t), \quad A = 1, 2. \qquad \text{(A.2)}$$

Obviously a set of tangent vectors $\boldsymbol{h}_A$ can be defined by

$$\boldsymbol{h}_A = \boldsymbol{x}_{,A} = x^i{}_{,A}\, \boldsymbol{e}_i = h^i{}_A\, \boldsymbol{e}_i\,, \qquad \text{(A.3)}$$

where the comma denotes partial derivation with respect to the surface coordinates z^A. These vectors $\boldsymbol{h}_A$ will be used as (covariant) surface base. With their aid the surface metric is calculated as follows:

$$h_{AB} = h_A{}^i\, h_B{}^i, \quad h = \det(h_{AB}). \qquad \text{(A.4)}$$

A unit normal to the surface S_t is introduced via the crossproduct from $\boldsymbol{h}_{\mathrm{I}}$ with $\boldsymbol{h}_{\mathrm{II}}$:

$$n_k = 0.5\, \varepsilon^{AB}\, \varepsilon_{kmp}\, h^m{}_A\, h^p{}_B\,, \quad k = 1, 2, 3\,.$$

ε^{AB} being the (surface) permutation tensor

$$\varepsilon^{AB} = h^{-1/2} \begin{cases} 1 & \\ -1 & \text{for} \\ 0 & \\ 0 & \end{cases} \begin{matrix} A = 1, B = 2, \\ A = 2, B = 1, \\ A = 1, B = 1, \\ A = 2, B = 2. \end{matrix}$$

With ε_{ijk} we denote the three-dimensional (cartesian) permutation tensor

$$\varepsilon^{ijk} = \begin{cases} 1 & \text{for } (i\,j\,k) \text{ an even permutation of } (123), \\ -1 & \text{for } (i\,j\,k) \text{ an odd permutation of } (123), \\ 0 & \text{else}. \end{cases}$$

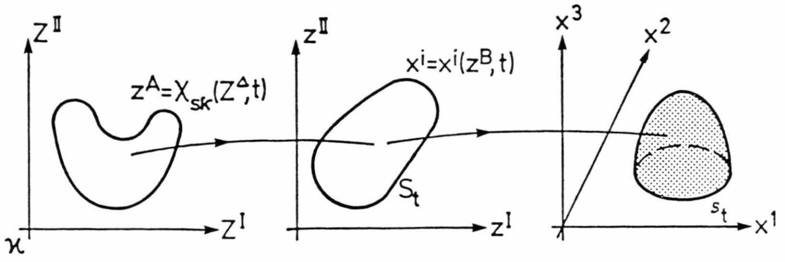

Fig. 5. Mappings and reference systems used to describe the motion of a two-dimensional continuum embedded in space. Z^Δ ($\Delta = 1, 2$) – coordinates of the reference configuration, z^A ($A = 1, 2$) – actual surface coordinates, x^i ($i = 1, 2, 3$) – actual space coordinates.

Additional structure is introduced by the concept of motion. If a fluid element in the surface moves with respect to the surface, the surface coordinates of this fluid element become a function of time,

$$z^A = \chi^A_{s\varkappa}(Z^\Delta, t), \tag{A.5.}$$

where $\varkappa$ refers to the particular reference-configuration (cf. Figure 5). The function $\chi^A_{s\varkappa}$ gives the surface parameters z^A of a point which was occupied at time t by a fluid element that may be identified with the parameters (material coordinates) Z^Δ in the reference-configuration $\varkappa$. (The reference-configuration may be visualized by e.g. the initial configuration.) The velocity of a fluid element with respect to the surface coordinates is accordingly given by

$$u^A = \left.\frac{\partial \chi^A_{s\varkappa}(Z^\Delta, t)}{\partial t}\right|_{Z^\Delta}.$$

The chain rule of differential calculus then gives the velocity in space

$$u^i = \left.\frac{\partial x^i}{\partial t}\right|_{Z^\Delta} = \left.\frac{\partial x^i}{\partial z^A}\right|_t \left.\frac{\partial z^A}{\partial t}\right|_{Z^\Delta} + \left.\frac{\partial x^i}{\partial t}\right|_{z^A} = u^A\, h_A{}^i + \left.\frac{\partial x^i}{\partial t}\right|_{z^A}.$$

The surface-coordinates may be chosen such that a point of s_t with fixed z^{I}, z^{II} moves only in direction of the unit normal $\boldsymbol{n}$ in space-coordinates,

$$\partial x^i / \partial t = u\, n^i, \tag{A.6}$$

u being the normal velocity of a point z^A of S_t resting on S_t.

In order to describe some properties of the surface one introduces fields on s_t, e.g. a mass or a momentum density. Such a field ϕ can be stated in terms of the material coordinates $\phi(Z^\Delta, t)$, in surface coordinates $\phi(z^A, t)$ or in space coordinates $\phi\,(x^i, t)$. With respect to curvilinear surface coordinates the covariant derivatives of a field $\phi(z^A, t)$ has the correct tensorial behaviour and is used instead of the usual partial derivative of a field $\phi(x_i, t)$ with respect to cartesian space coordinates. As an example the covariant derivative of a contravariant vector field is given:

$$\begin{aligned} \boldsymbol{\Phi}_{,A} &= (\Phi^B{}_{,A} + \{{}^B{}_{AC}\}\, \Phi^C)\, \boldsymbol{h}_B + \Phi^B\, \Omega_{AB}\, \boldsymbol{n} \\ &=: \boldsymbol{h}_B\, \Phi^B{}_{;A} + \Phi^B\, \Omega_{AB}\, \boldsymbol{n} \end{aligned} \tag{A.7}$$

with the Christoffel symbols

$$\{{}^A{}_{BC}\} = \boldsymbol{h}_{B,C}\, \boldsymbol{h}^A. \tag{A.8}$$

The covariant derivative of the surface basis yields

$$\boldsymbol{h}_{A;B} = \Omega_{AB}\, \boldsymbol{n} \tag{A.9}$$

with the second fundamental form

$$\Omega_{AB} = \boldsymbol{h}_{A,B}\, \boldsymbol{n}\,. \tag{A.10}$$

The Gaussian curvature K_{G} and the mean curvature K_{M} are defined by

$$K_{\mathrm{G}} = \det(\boldsymbol{\Omega}), \quad K_{\mathrm{M}} = \tfrac{1}{2}\,\mathrm{tr}\,(\boldsymbol{\Omega}), \tag{A.11}$$

respectively.

[1] B. Chapman, Glow Discharge Processes, John Wiley, New York 1980.
[2] H. K. Kuiken, J. J. Kelly, and P. H. L. Notten, J. Electrochem. Soc. **133,** 6, 1217 (1986).
[3] J. Stefan, Ann. Phys. Chem. **42,** 269 (1891).
[4] C. Bowen, Arch. Rat. Mech. Anal. **53,** 277 (1974).
[5] A. W. Adamson, Physical Chemistry of Surfaces, John Wiley, New York 1982.
[6] I. Müller, Thermodynamik, Bertelsmann Universitätsverlag, Düsseldorf 1973.
[7] R. M. Bowen, Theory of Mixtures, in: Continuum Physics 3, ed. A. C. Eringen. Academic Press, New York-London 1971.
[8] R. Aris, Vectors, Tensors, and the Basic Equations of Fluid Mechanics, Prentice Hall, Englewood Cliffs 1962.
[9] J. Kovac, Physica **86 A,** 1 (1977).
[10] L. Waldmann, Z. Naturforsch. **22a,** 1269 (1967).
[11] J. Meixner and H. G. Reik, Thermodynamik der irreversiblen Prozesse, in: Handbuch der Physik III/2, ed. by S. Flügge, Springer-Verlag, Berlin 1959.
[12] D. Bedeaux, A. M. Albano, and P. Mazur, Physica **82a,** 438 (1976).
[13] F. Vodák, Physica **93 A,** 244 (1978).
[14] P. A. Wolff and A. M. Albano, Physica **98 A,** 491 (1979).
[15] G. M. C. Fisher and M. J. Leitman, Arch. Rat. Mech. Anal. **30,** 225 (1968).
[16] G. M. C. Fisher and M. J. Leitman, Quart. Appl. Math. **28,** 3, 303 (1970).
[17] G. P. Moeckel, Arch. Rat. Mech. Anal. **57,** 255 (1975).
[18] H. Cohen and C. C. Wang, Arch. Rat. Mech. Anal. 1982, 205.
[19] I. S. Liu and I. Müller, Arch. Rat. Mech. Anal. **46** (2), 149 (1972).
[20] R. Benach and I. Müller, Arch. Rat. Mech. Anal. **53,** 312 (1973/74).
[21] C. Truesdell and R. Toupin, The Classical Field Theories, Handbuch der Physik III/1, ed. by S. Flügge, Springer-Verlag, Berlin 1960.
[22] C. C. Wang, Arch. Rat. Mech. Anal. **36,** 166 (1970).
[23] H. Wallschläger, Zur Thermodynamik bewegter Ränder und eine Anwendung zum Plasmaätzen, Dissertation, TU Braunschweig 1986.
[24] S. de Groot and P. Mazur, Non Equilibrium Thermodynamics, North-Holland, Amsterdam 1963.
[25] C. Truesdell, Rational Thermodynamics, Springer-Verlag, New York 1984.
[26] I. Müller, J. Mécan. **2,** 267 (1975).
[27] I. S. Liu, Arch. Rat. Mech. Anal. **46,** 2, 131 (1972).
[28] A. M. Albano and D. Bedeaux, Physica **147 A,** 407 (1987).
[29] A. Grauel, Physica **103 A,** 468 (1980).
[30] G. Bowen, Int. J. Eng. Sci. **8,** 63 (1970).