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On Jump Conditions at Phase Boundaries for Ordered and Disordered Phases

Wolfgang Dreyer

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Weierstrass-Institute
for Applied Analysis
and Stochastics
Mohrenstr. 39
10117 Berlin
Germany
E-Mail: dreyer@wias-berlin.de

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Edited by
Weierstraß-Institut für Angewandte Analysis und Stochastik (WIAS)
Mohrenstraße 39
D — 10117 Berlin
Germany

Fax: + 49 30 2044975
E-Mail: preprint@wias-berlin.de
World Wide Web: http://www.wias-berlin.de/

Abstract

This is a study on jump conditions across the interface between two adjacent phases. The interface behaves as a free boundary, and in sharp interface models jump conditions are used to determine the values of thermodynamic fields at the free boundaries.

In this study the jump conditions are derived from balance equations for singular surfaces that do not have singular lines, i.e. triple junctions are not considered here. At first we present the most general form of jump conditions to give a general framework, from where we consider various special cases with a focus on the influence of mechanical fields on the interfacial processes. The special cases include the Hoffmann/Cahn capillarity vector theory and jump conditions for interfaces where order/disorder transitions are involved. Furthermore we discuss interfacial chemical reaction laws, and in particular the creation and annihilation of vacancies at a liquid/solid interface.

1 Introduction

An example for the need of interfacial jump conditions is given by stress assisted diffusion in single crystal Gallium Arsenide (GaAs) that leads to the formation and growth of unwanted liquid droplets in a solid surrounding, [9], [36], and [37]. The modeling of this thermodynamic process relies in its essential parts on jump conditions at the liquid/solid interface. There is already an extensive literature on jump conditions, see in particular [2], [27], [26], [16], [22], [3], and [17] for a general thermodynamic treatment, [24], where pure mechanical jump conditions are derived and [25] where exclusively the Stefan jump condition is explored. However, the jump conditions that appropriately represent the phenomena of the described example are not among the results from the literature, because these ignore order/disorder transitions and the creation and annihilation of vacancies are also not considered.

Here the general objective is a study on the interface between two adjacent bodies. Different kinds of interfaces may appear: (i) Phase boundaries: The interface separates two phases of a single substance, say liquid and gas. A more complex example is as follows. The interface separates two phases consisting of a mixture of several constituents. Some of them may cross the interface, while it behaves impermeable for other constituents. Interfacial chemical reactions may also happen, so that incoming constituents are created or annihilated on the interface. (ii) Contact areas: Two adjacent bodies are made from different materials, say copper in contact with steel. In this case often only mechanical forces are transmitted across the interface. (iii) Membranes and shells: It may happen, that the interface between two adjacent bodies is in fact a thin body. In the zero thickness limit, the thin body can usually be represented by a surface, which is called *membrane* or *shell*, respectively. A rubber balloon which separates two gases provides a well known example for a membrane.

In this study we are especially interested in phase boundaries, however, many of the calculated relations are also valid for contact areas and thin bodies. In the following we will use the general notion *interface.* Sometimes the interface is called a *singular surface*, because in general the interfacial limit values of the thermodynamic fields of the adjacent bodies are discontinuous, when they are formed from different sides of the interface.

There are different strategies to derive jump conditions. They can be established by minimization of the Gibbs free energy, see Alexander & Johnson, [2], for a quite general treatment in case that fluids and only disordered solids are involved, and Dreyer & Duderstadt, [9], where a plane interface between a liquid and the ordered solid, viz. semi-insulating GaAs, is considered. In the current study the interfacial jump conditions rely on global equations of balance for a test volume $V = V_+ \cup V_-$, where the partial volumes V_+ and V_- are occupied by two phases of a material body consisting of $a_c^{+/-}$ chemically different constituents. For disordered solids, the same strategy is explored by Gurtin and Voorhees, [17], [18], however, these authors additionally introduce the so called configurational forces. These quantities are avoided in the following.

The thermodynamic constitutive theory of chemically reacting mixtures is not among the objectives of this study. However, even so we need some thermodynamic relations for the bulk materials: the Gibbs equation, the Gibbs/Duhem equation, and the relation between energy and entropy flux. The underlying thermodynamic mixture theory is carefully and extensively developed and discussed in [27] and [28] by Ingo Müller. The few necessary generalizations to mixtures of solids are explicitly given in the current study.

In the past, the anisotropy of interfaces is often described by the capillarity vector ξ according to Cahn & Hoffmann, [20], [21]. In Section 13.2 we relate ξ to the normal component of the surface stress vector and we show that its appearance induce a non-conserved interfacial angular momentum. The Cahn/Hoffmann jump conditions ignore interfacial elasticity and deviatoric stresses of the bulk materials. Both phenomena are included in the corresponding jump conditions of the current study.

In contrast to disordered solids there are privileged lattice sites in ordered solids, and this phenomenon is described by a partition of the crystal lattice into various sublattices. Interfacial jump conditions must determine the distribution of the constituents on the sublattices at a, say, liquid/ordered solid interface. They are thus different from jump conditions that describe a liquid/disordered solid interface. Both cases are discussed in detail in Sections 15.3 and 15.4.

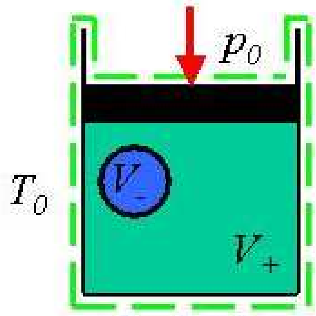

Figure 1: Device for demonstration of the Gibbs/Thomson law

2 The content of the classical Gibbs/Thomson law

The most well known jump conditions concern the interface between a liquid droplet and vapour, and determine (i) the pressure jump at the interface and (ii) the vapour pressure by the curvature of the droplet. The equations are known as the Gibbs/Thomson law, [34], [15]. In order to illustrate the content of the Gibbs/Thomson law we consider the system from Figure 1. A pressure vessel is closed by a movable piston and contains a spherical liquid droplet with radius r consisting of a single substance in contact with its vapour at uniform temperature T_0 and constant outer pressure p_0.

The conditions of (unstable) equilibrium are, see [27], [28], [10] for details,

$$p_+ = p_0, \quad p_- = p_+ + \frac{2\sigma}{r}, \quad g_+(T_0, p_+) = g_-(T_0, p_-). \tag{1}$$

Here σ is the surface tension and the functions $g_{+/-}$ denote the specific Gibbs free energies of vapour and liquid, respectively. In sections 13.1 and 15.3.2 the laws $(1)_2$ and $(1)_3$ will be rederived.

The conditions $(1)_{1,2}$ describe mechanical equilibrium, while $(1)_3$ determines thermodynamic equilibrium. The condition $(1)_2$ relates the pressure difference to the curvature of the droplet and was first formulated by Laplace, [23]. In $(1)_3$ we may eliminate the liquid pressure by means of $(1)_2$. If we consider an incompressible liquid, i.e. $\partial v/\partial p = 0$, where v is the specific volume of the liquid, we obtain due to $(\partial g/\partial p) = v$

$$g_+(T_0, p_+) - g_-(T_0, p_+) = v_- \frac{2\sigma}{r}. \tag{2}$$

This is the classical Gibbs Thomson law, which can be used to calculate the vapour pressure p_+ as a function of temperature and curvature of the droplet.

It is important to compare $(1)_3$ with (2). Both laws have the same content. However, the pressure arguments in $(1)_3$ correspond to the vapour phase and liquid phase, respectively, while in (2) the vapour pressure appears in g_+ as well as in g_-. The pressure difference between liquid and vapor is explicitly given on the right hand side of (2).

A simple kinetic consideration allows even the calculation of a growth law for the droplet, [10]. It reads

$$\begin{aligned}\frac{dr}{dt} = v_- \sqrt{\frac{kT_0}{2\pi m}} \frac{p_V(T_0)}{kT_0} \exp(\frac{m(g_+(T_0,p_+) - g_-(T_0,p_+))}{kT_0}) \times \\ \times \left(1 - \exp(\frac{m(g_+(T_0,p_+) - g_-(T_0,p_-))}{kT_0})\right)\end{aligned} \tag{3}$$

The newly introduced quantities are the atomic mass, m, the Boltzmann constant, k, and the vapour pressure, p_V, that corresponds to a flat interface. The vapour pressure p_V solves (2) for $r \to \infty$.

For a given initial radius $r(0)$, the growth law determines the evolution of the droplet. For given T_0, p_0, we can calculate from $g_+(T_0,p_0) - g_-(T_0,p_0) = v_- 2\sigma/r_c$ a critical radius r_c, and for $r(0) < r_c$ the droplet will shrink while it will grow for $r(0) > r_c$.

Finally we give a simple calculation that relates the surface tension to the free energy density of the interface. To this end we calculate the necessary work to change the total volume of the system in an isothermal process. This work is equal to a change of the total free energy Ψ. We write

$$\begin{aligned}d\Psi = -p_+ dV = -p_+ d(V_+ + V_-) = -p_+ dV_+ - p_- dV_- + (p_- - p_+)dV_- = \\ = d\Psi_+ + d\Psi_- + \sigma da,\end{aligned} \tag{4}$$

where $a = 4\pi r^2$ is the surface of the droplet. We conclude that the total change of the free energy consists of three parts corresponding to the two bulk phases and to the interface. In particular we may identify $d\Psi_s = \sigma da$, where $d\Psi_s$ gives the isothermal change of the interfacial free energy Ψ_s.

A slight generalization of this result can be obtained as follows: Let T_s and S_s denote surface temperature and surface entropy, respectively, and let us assume that a change of T_s gives rise to a change of the surface free energy in the usual manner, so that there results an interfacial Gibbs equation, viz.

$$d\Psi_s = -S_s dT_s + \sigma da. \tag{5}$$

There follows

$$S_s = -\frac{\partial \Psi_s}{\partial T_s}, \quad \sigma = \frac{\partial \Psi_s}{\partial a} \quad \text{and the integrability condition} \quad \frac{\partial S_s}{\partial a} = -\frac{\partial \sigma}{\partial T_s}. \tag{6}$$

Furthermore let us consider a small surface element a with a uniform distribution of temperature T_s, and let us assume

$$\Psi_s = \psi_s(T_s)a, \quad S_s = s_s(T_s)a. \tag{7}$$

We conclude

$$\sigma = \psi_s, \quad s_s = -\frac{\partial \sigma}{\partial T_s}, \tag{8}$$

and this form of the interfacial contribution to the free energy is the historical reason to call the introduced *surface tension* σ also *interfacial free energy density*.

The described model is obviously too simple in many circumstances. For example, rubber membranes do not behave in this simple way, see [8], [11] for details. Furthermore, interfaces that represent phase boundaries are also not adequately described by this model if anisotropic solids are involved. In Section 12 we will generalize this result to anisotropic and elastic deformable surfaces.

Atomistic models for the calculation of the surface tension are found to be in [8] for elastic membranes, in [32] for fluid/fluid interfaces and in [33], where the calculation starts from a lattice model.

3 A piece of thermodynamics for liquids and solids

3.1 Euler and Lagrange description of the variables

We consider a body B whose volume $V(t)$ may depend on time t. We may use a fixed Cartesian coordinate system to indicate a space point, which at some time t is occupied by a *material point* P of B, by its Cartesian coordinates $x = (x^i) = (x^1, x^2, x^3)$. The notion *material point* means the smallest units of B that cannot further be resolved on the chosen space scale.

If the body B is a mixture of a_c constituents, the variables to describe the thermodynamic state of B are the fields

$$\begin{aligned}
\rho_a &= \rho_a(t,x), \quad a \in \{1,2,...,a_c\}, && \text{partial mass densities,} \\
v^i &= v^i(t,x), && \text{barycentric velocity of the mixture,} \\
u &= u(t,x), && \text{specific internal energy of the mixture.}
\end{aligned} \tag{9}$$

The total mass density of the mixture, ρ, is given by the sum over the partial mass densities, and for some purposes it is useful to calculate the mixture velocity, v^i, from the velocities of the constituents, v^i_a. Thus we write

$$\rho = \sum_{a=1}^{a_c} \rho_a \quad \text{and} \quad v^i = \sum_{a=1}^{a_c} \frac{\rho_a}{\rho} v^i_a. \tag{10}$$

The given description of B is called spatial or Euler description, and we call the pair (t,x) Euler coordinates.

In order to describe the deformation of the considered body, it is useful to indicate any material point P of B at a fixed reference time t_0 by its coordinates $X = (X^i) = (X^1, X^2, X^3)$ with respect to a rectangular Cartesian coordinate system.

The motion of the point P, is then described by the field $\chi(t,X) = \chi^i(t,X) = (\chi^1(t,X),\ \chi^2(t,X), \chi^3(t,X))$, which gives the coordinates of P at time $t > t_0$:

$$x^i = \chi^i(t,X). \tag{11}$$

The field χ is called *motion*, and its first derivatives

$$\hat{\upsilon}^i = \frac{\partial \chi^i}{\partial t} \qquad \text{and} \qquad F^{ij} = \frac{\partial \chi^i}{\partial X^j} \qquad \text{with} \qquad J = \det(F^{ij}) \neq 0 \tag{12}$$

are the *velocity* and the *deformation gradient*, respectively. The condition on the Jacobian J guarantees that (11) is invertible.

Later on, we will need an identity, that reads

$$\frac{\partial}{\partial X^k}(J\overset{-1}{F}{}^{ki}) = 0. \tag{13}$$

This identity follows from the definitions (12) by a straightforward calculation.

If the body B is a mixture consisting of a_c constituents, the variables are the fields of motion, partial mass densities and internal energy, respectively,

$$x^i = \chi^i(t, X), \quad \rho_a = \hat{\rho}_a(t, X), \quad u = \hat{u}(t, X). \tag{14}$$

The description of the body B by fields that map the coordinates X into some function space, is called material or Lagrange description, and we call the pair (t, X) Lagrange coordinates.

We may use the field of motion to relate the Euler description to the Lagrange description by

$$\hat{\rho}_a(t, X) = J\rho_a(t, \chi(t, X)), \quad \hat{\upsilon}^i(t, X) = \upsilon^i(t, \chi(t, X)), \qquad \hat{u}(t, X) = Ju(t, \chi(t, X)). \tag{15}$$

The Lagrange description is quite natural for solids whereas in liquids and gases the Euler description is more convenient. In this study on interfacial boundary conditions, both descriptions are needed, because it often happens that the adjacent substances at an interface are liquid and solid.

3.2 Gibbs equation for fluids and solids as bulk materials

There are further important quantities to describe properties of mixtures. These are: temperature, T, specific entropy, s, free energy, $\psi = u - Ts$, and the chemical potentials of the constituents, μ_a, [27], [28].

Furthermore there are three measures of stress, viz. the Cauchy stress, σ^{ik}, and the first and second Piola Kirchhoff stress, respectively, $\hat{\sigma}^{ik}$ and t^{ik}:

$$\sigma^{ik} = \sigma^{ki}, \quad \hat{\sigma}^{ik} = J\overset{-1}{F}{}^{ij}\sigma^{jk}, \quad t^{ik} = J\overset{-1}{F}{}^{ij}\overset{-1}{F}{}^{kl}\sigma^{jl}. \tag{16}$$

The Cauchy stress appears naturally in the Euler description, the first Piola Kirchhoff stress is a measurable quantity, and appears naturally in the Lagrange description. Finally the second Piola Kirchhoff stress is needed to formulate constitutive laws, which relate the stress to the variables, [35]. Let us decompose the Cauchy stress into its trace and the traceless part, the latter one is indicated by angle brackets around the indices. We write

$$\sigma^{ik} = -p\delta^{ik} + \sigma^{<ik>} \quad \text{with} \quad p = -\frac{1}{3}\sigma^{nn}, \tag{17}$$

and we call the quantity p the pressure.

There also are various measures of the deformation of a body. An important one is the right Cauchy Green tensor, C^{ik}, and its unimodular restriction, which we denote by c^{ik}:

$$C^{ik} = F^{mi}F^{mk} \quad \text{and} \quad c^{ik} = J^{-3/2}C^{ik} \quad \text{so that} \quad \det(c^{ik}) = 1. \tag{18}$$

All these quantities are related to each other by the Gibbs equation, which read in fluids as well as in thermoelastic solids

$$d\rho\psi = -\rho s dT + \frac{1}{2}J^{-1/3}t^{ik}dc^{ik} + \sum_{a=1}\mu_a d\rho_a. \tag{19}$$

The Gibbs equation implies

$$\rho s = -\frac{\partial\rho\psi}{\partial T}, \quad t^{ik} = 2J^{1/3}\frac{\partial\rho\psi}{\partial c^{ik}}, \quad \text{and} \quad \mu_a = \frac{\partial\rho\psi}{\partial\rho_a}. \tag{20}$$

Furthermore, there holds the Gibbs/Duhem equation

$$p = -\rho\psi + \sum_{a=1}\mu_a\rho_a. \tag{21}$$

We conclude that the knowledge of the free energy density $\rho\psi(T, \rho_1,...,\rho_{a_c}, c^{ik})$ is sufficient to calculate all the introduced quantities. In this study, we assume the free energy density to be given.

In a mixture of isotropic fluids the free energy does not depend on c^{ik}, and the second Piola/Kirchhoff stress drops out of the Gibbs equation. Thus for a fluid phase the knowledge of the free energy density $\rho\psi(T, \rho_1,...,\rho_{a_c})$ is sufficient to relate the introduced quantities to the variables.

The proof of the Gibbs equation and of the Gibbs/Duhem equation for fluid mixtures and for those solids that only consist of a single substance can be found in [27]. The generalization to a solid mixture, viz. eqns. (19) and (21), has not been published elsewhere, but it can be derived along the strategies that are outlined by I. Müller in [27].

3.3 Entropy flux/heat flux relation

Later on we need a further result of thermodynamics of mixtures, which gives the relation between the entropy flux, ϕ^k, and the heat flux, q^k. In a chemically reacting mixture of fluids and even in solids, which may be exposed to the influence of mechanical stress fields, the entropy flux/heat flux relation is given by

$$\phi^k = \frac{1}{T}(q^k - \sum_{a=1}^{a_c} \mu_a J_a^k). \tag{22}$$

Here J_a^k denote the components of the diffusion flux of the constituents, see [27] and [9] for details.

4 Singular surfaces

The common boundary between two adjacent phases is described by a surface $\mathfrak{s}$. We call $\mathfrak{s}$ a singular surface, because the thermodynamic fields may suffer discontinuities if the phase boundary is crossed. The conditions that relate the limiting values of the fields at a singular surface are called jump conditions.

4.1 Various descriptions of surfaces

In Euler coordinates a surface $\mathfrak{s}$ may be described by the equation

$$\mathfrak{s}(t, x) = 0. \tag{23}$$

Under some assumptions, we may also describe $\mathfrak{s}$ in Lagrange coordinates.

Throughout this study, we consider exclusively so called *coherent interface boundaries*. These are defined by a field of motion which is continuous across the surface $\mathfrak{s}$. Thus we are allowed to use $x^i = \chi^i(t, X)$ to describe $\mathfrak{s}$ in the reference configuration according to

$$\hat{\mathfrak{s}}(t, X) := \mathfrak{s}(t, \chi(t, X)) = 0. \tag{24}$$

There are two more possibilities to describe the geometry of a surface. To this end we introduce Gaussian parameters U^Γ, $\Gamma \in \{1, 2\}$ and describe the surface by

$$x_s^i = \hat{x}_s^i(t, U^\Gamma) \quad \text{and} \quad X_s^i = \hat{X}_s^i(t, U^\Gamma) \tag{25}$$

in the actual and in the reference configuration, respectively.

4.2 Euler and Lagrange description of surfaces

We consider the surface in Euler coordinates and assign to each point of the surface a normal vector, ν^i, and its normal speed, w_ν, respectively. In Lagrange coordinates we write N^i and W_N. The normal vectors can be calculated from (23) and (24) by

$$\nu^i = \frac{\mathfrak{s}_{x_i}}{\sqrt{\mathfrak{s}_{x_k}\mathfrak{s}_{x_k}}} \quad \text{and} \quad N^i = \frac{\hat{\mathfrak{s}}_{X_i}}{\sqrt{\hat{\mathfrak{s}}_{X_k}\hat{\mathfrak{s}}_{X_k}}}, \tag{26}$$

while the normal speeds follow according to

$$w_\nu = -\frac{\mathfrak{s}_t}{\sqrt{\mathfrak{s}_{x_k}\mathfrak{s}_{x_k}}} \quad \text{and} \quad W_N = -\frac{\hat{\mathfrak{s}}_t}{\sqrt{\hat{\mathfrak{s}}_{X_k}\hat{\mathfrak{s}}_{X_k}}}. \tag{27}$$

Here partial derivatives are indicated by indices.

The side of $\mathfrak{s}$ into which the normal points is called the "+" region, the other side is the "-" region. The brackets

$$[[\psi]] = \psi_+ - \psi_- \qquad \text{and} \qquad \{\psi\} = \frac{1}{2}(\psi_+ + \psi_-), \tag{28}$$

denote the jump and the mean value of any generic quantity ψ, where $\psi_{+/-}$ represent the limiting values of ψ formed in the "+" region and "-" region, respectively:

$$\psi_{+/-} = \lim_{x \in \text{``}+/-\text{''},\, x \to x^s} \psi(t, x). \tag{29}$$

The continuity condition, $[[\chi_i]] = 0$, implies that the temporal and spatial derivatives of χ_i, giving the velocity v_i and the deformation gradient F_{ij}, obeys the Hadamard conditions

$$[[v_i]] = -W_N[[F_{ij}]]N_j, \quad [[F_{ij}]] = a_i N_j. \tag{30}$$

A proof of (30) is found in [35].

4.3 Gaussian description of surfaces

Another possible description of the surface $\mathfrak{s}$ results by the introduction of Gaussian surface parameters U^Γ, $\Gamma \in \{1, 2\}$, so that any point P on $\mathfrak{s}$ is indicated by the function $x^i_s = \hat{x}^i_s(t, U^\Gamma)$. In P we define tangential vectors, the metric tensor and the the normal vector, respectively, according to

$$\tau^i_\Gamma = \frac{\partial \hat{x}^i_s}{\partial U^\Gamma}, \quad g_{\Delta\Gamma} = \tau^i_\Delta \tau^i_\Gamma, \quad \nu^i = \frac{\varepsilon^{ijk}\tau^j_1\tau^k_2}{\sqrt{g}}, \quad \text{with} \quad g = \det(g_{\Delta\Gamma}). \tag{31}$$

The spatial derivative of τ^i_Γ may be decomposed with respect to tangential and normal components as

$$\frac{\partial \tau^i_\Gamma}{\partial U^\Delta} = \Gamma^\Lambda_{\Gamma\Delta}\tau^i_\Lambda + b_{\Gamma\Delta}\nu^i \quad \text{with} \quad \Gamma^\Lambda_{\Gamma\Delta} = g^{\Lambda\Sigma}\frac{\partial \tau^i_\Gamma}{\partial U^\Delta}\tau^i_\Sigma \quad \text{and} \quad b_{\Gamma\Delta} = \frac{\partial \tau^i_\Gamma}{\partial U^\Delta}\nu^i. \tag{32}$$

The quantities $\Gamma^\Lambda_{\Gamma\Delta}$ and $b_{\Gamma\Delta}$ are the Christoffel symbols and the curvature tensor, respectively. The spatial derivative of the normal vector ν^i can be calculated to

$$\frac{\partial \nu^i}{\partial U^\Delta} = -g^{\Sigma\Gamma} b_{\Delta\Gamma}\tau^i_\Sigma. \tag{33}$$

The mean curvature k_M is defined by

$$k_M = \frac{1}{2} b_{\Gamma\Delta} g^{\Gamma\Delta}. \tag{34}$$

Next we define the speed w^i of $\mathfrak{s}$ and its decomposition into tangential and normal parts by

$$w^i = \frac{\partial \hat{x}_i^s}{\partial t} = w_\tau^\Gamma \tau_\Gamma^i + w_\nu \nu^i. \tag{35}$$

The calculation of the spatial derivative of w^i yields

$$\frac{\partial w^i}{\partial U^\Delta} = (w_{\tau;\Delta}^\Gamma - w_\nu g^{\Gamma\Sigma} b_{\Sigma\Delta})\tau_\Gamma^i + (\frac{\partial w_\nu}{\partial U^\Delta} + w_\tau^\Gamma b_{\Gamma\Delta})\nu^i, \tag{36}$$

where the semicolon denotes covariant derivatives.

For later use we need the time derivatives of the metric tensor and the normal vector, which can also easily be calculated. They read

$$\frac{\partial g_{\Delta\Gamma}}{\partial t} = w_{\tau;\Delta}^\Sigma g_{\Gamma\Sigma} + w_{\tau;\Gamma}^\Sigma g_{\Delta\Sigma} - 4 w_\nu k_M \quad \text{and} \quad \frac{\partial \nu^i}{\partial t} = -(\frac{\partial w_\nu}{\partial U^\Gamma} + w_\tau^\Sigma b_{\Sigma\Gamma}) g^{\Gamma\Delta} \tau_\Delta^i. \tag{37}$$

Obviously we likewise may start from the function $\hat{X}_s^i(t, U^\Gamma)$ in order to describe the surface $\mathfrak{s}$ with respect to Lagrange coordinates. In this case we end up with formulas that have the same structure as above, but in order to indicate the Lagrange description, all quantities are now written with capital letters. For example, we write

$$W^i = \frac{\partial \hat{X}_i^s}{\partial t}, \quad T_\Gamma^i = \frac{\partial \hat{X}_i^s}{\partial U^\Gamma}, \quad G_{\Delta\Gamma} = T_\Delta^i T_\Gamma^i, \quad G = \det(G_{\Delta\Gamma}), \tag{38}$$

and the other quantities are defined accordingly.

There are simple relations involving normal vectors and interfacial speeds of both descriptions. These read

$$N^k = \sqrt{\frac{g}{G}} \frac{1}{J^{+/-}} F_{+/-}^{ik} \nu^i, \quad w^i = v_{+/-}^i + F_{+/-}^{ik} W^k, \quad W_N = \sqrt{\frac{g}{G}} \frac{1}{J^{+/-}} (w_\nu - v_{+/-}^k \nu^k). \tag{39}$$

We may conclude from $(39)_1$ that the expression $J\overset{-1}{F}{}^{ki} N^k$ is continuous across the surface:

$$[[J\overset{-1}{F}{}^{ki}]] N^k = 0. \tag{40}$$

Later on this identity will be used to transform the jump conditions between the Euler- and the Lagrange description.

5 General equations of balance

The general equations of balance will be formulated for a material volume, which has the property that no mass flux through its boundary ∂V is allowed. In other

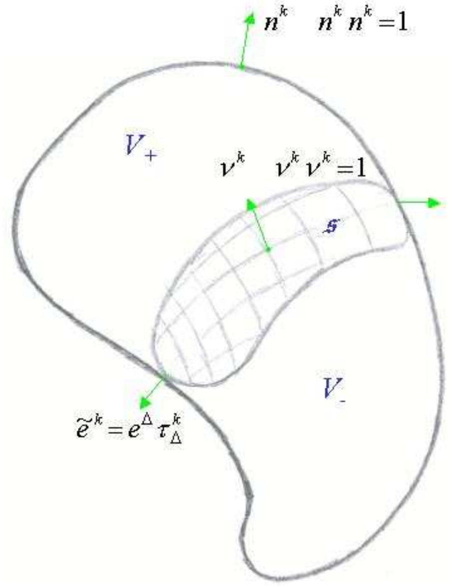

Figure 2: A material volume is divided into two parts by a singular surface

words: The boundary of a material volume moves with the velocity of the particles of the body. A material volume is useful to describe the global equations of balance.

Figure 2 shows a material volume which is decomposed into two regions with volumes V_+ and V_- by a singular surface $\mathfrak{s}$. The normal vector of the material surfaces ∂V_+ , ∂V_- and of the singular surface are denoted by n^k and ν^k, respectively. The unit vector $\tilde{e}^k = e^\Delta \tau^k_\Delta$ indicates a vector which is tangential to $\mathfrak{s}$ and normal to $\partial\mathfrak{s}$.

Note that ∂V_+ , ∂V_- are material surfaces, so that no mass flux is allowed through ∂V_+ , ∂V_-, while the singular surface $\mathfrak{s}$ is generally not material, so that the exchange of mass between the volumes V_+ and V_- is possible.

5.1 General global equation of balance

We consider the volume, which is indicated in Figure 2 and formulate the general equation of balance for a generic additive quantity Ψ:

$$\frac{d\Psi}{dt} = \text{Flux}(\Phi) + \text{Source}(\Xi). \tag{41}$$

The quantity Ψ may have a volume density ψ_v and a surface density ψ_s, and we decompose Ψ as

$$\Psi = \int\limits_{V_+ + V_-} \psi_v d^3x + \int\limits_{\mathfrak{s}} \psi_s da. \tag{42}$$

Accordingly we introduce a volume flux density φ_v^k and surface flux density $\tilde{\varphi}_s^k = \varphi_s^\Delta \tau_\Delta^k$ in order to decompose the flux Φ of Ψ through $\partial V_+ \backslash \mathfrak{s}$, $\partial V_- \backslash \mathfrak{s}$ and through $\partial \mathfrak{s}$:

$$\Phi = -\int\limits_{\partial V_+ \backslash \mathfrak{s}} \varphi_v^k \nu_k da - \int\limits_{\partial V_- \backslash \mathfrak{s}} \varphi_v^k \nu_k da - \int\limits_{\partial \mathfrak{s}} \varphi_s^\Delta e_\Delta dl. \tag{43}$$

The first two contributions to the flux describe nonconvective fluxes across the material surfaces $\partial V_+ \backslash \mathfrak{s}$, $\partial V_- \backslash \mathfrak{s}$, while the third contribution describes a flux, which is tangential to $\mathfrak{s}$ and normal to its boundary $\partial \mathfrak{s}$. The sign is chosen, so that incoming fluxes induce positive contributions to Φ.

Let Ξ be the source of Ψ with volume density ξ_v and surface density ξ_s:

$$\Xi = \int\limits_{V_+ + V_-} \xi_v d^3x + \int\limits_{\mathfrak{s}} \xi_s da. \tag{44}$$

The general equation of balance (41) thus read

$$\begin{aligned} \frac{d}{dt}\Big(\int\limits_{V_+ + V_-} \psi_v d^3x + \int\limits_{s} \psi_s da\Big) = -\int\limits_{\partial V_+ \backslash \mathfrak{s}} \varphi_v^k n_k da - \int\limits_{\partial V_- \backslash \mathfrak{s}} \varphi_v^k n_k da - \int\limits_{\partial \mathfrak{s}} \varphi_s^\Delta e_\Delta dl + \\ \int\limits_{V_+ + V_-} \xi_v d^3x + \int\limits_{\mathfrak{s}} \xi_s da. \end{aligned} \tag{45}$$

Next we will exploit (45) separately for points lying in $V_\pm$ and $\mathfrak{s}$, respectively. To this end we need so called *transport theorems*, which are rules to interchange the time differentiation in (45) with the appearing time dependent volume and surface integrals.

5.2 Transport theorems for volume and surface integrals, surface divergence theorem

The identity

$$\frac{d}{dt}\int\limits_{V_+ + V_-} \psi_v d^3x = \int\limits_{V_+ + V_-} \frac{\partial \psi_v}{\partial t} d^3x + \int\limits_{\partial V_+ \backslash \mathfrak{s} \cup \partial V_- \backslash \mathfrak{s}} \psi_v v^k n^k da \mp \int\limits_{\mathfrak{s}} [[\psi_v]] w_\nu da, \tag{46}$$

is called transport theorem for volume integrals, and its proof is an immediate consequence of Reynolds transport theorem for volume integrals for a region with volume Ω, whose surface $\partial\Omega$ moves with the velocity w_k, see [27], [4], and [35] for details,:

$$\frac{d}{dt}\int\limits_{\Omega} \psi_v d^3x = \int\limits_{\Omega} \frac{\partial \psi_v}{\partial t} d^3x + \int\limits_{\partial \Omega} \psi_v w^k n^k da. \tag{47}$$

In order to formulate the transport theorem for surface integrals, we assume at first that the surface fields are given as functions of Gaussian surface parameters U^Γ, $\Gamma \in \{1, 2\}$. The transport theorem for surface integrals is the identity

$$\frac{d}{dt}\int\limits_{\mathfrak{s}} \psi_s da = \int\limits_{\mathfrak{s}} (\frac{\partial \psi_s(t, U^\Gamma)}{\partial t} + \psi_s(w^\Delta_{\tau;\Delta} - 2k_M w_\nu))da, \tag{48}$$

and its proof is given in [4] and [27] .

Finally there is a divergence theorem for surfaces, which reads

$$\int\limits_{\mathfrak{s}} \varphi^\Delta_{;\Delta} da = \oint\limits_{\partial\mathfrak{s}} \varphi^\Delta e_\Delta dl. \tag{49}$$

The proof of the identity (49) relies on the three-dimensional Stokes theorem, and its proof can also be found in [4] and in [27].

5.3 General local equation of balance in Euler coordinates

The following local versions of the global balance (45) will be given here in Euler coordinates. The transition to Lagrange coordinates will be carried out in Section 5.4.

In regular points, i.e. $x \in V_\pm$, the local version of (45) reads

$$\frac{\partial \psi_v}{\partial t} + \frac{\partial}{\partial x_k}(\psi_v v^k + \varphi^k_v) = \xi_v. \tag{50}$$

The proof relies on (46), which will be applied to an arbitrary material volume that is contained in, V_+ and V_-, respectively.

Regarding points, lying on the singular surface $\mathfrak{s}$, the local version of (45) reads

$$-w_\nu[[\psi_v]] + [[\psi_v v^k + \varphi^k_v]]\nu_k = -\frac{\partial \psi_s(t, U^\Gamma)}{\partial t} - \psi_s(w^\Delta_{\tau;\Delta} - 2k_M w_\nu) - \varphi^\Delta_{s;\Delta} + \xi_s. \tag{51}$$

The proof of eqn. (51) relies on the so called *pillbox argument*: The global equation of balance (45) is applied to the cylindrical volume of Figure 3. The limit $H \to 0$ implies immediately the eqn. (51).

The generic equations (50) and (51) set the general frame of equations of balance. The conservation laws for mass, momentum, energy and further special equations of balance follow by special choices for the generic densities, fluxes and productions.

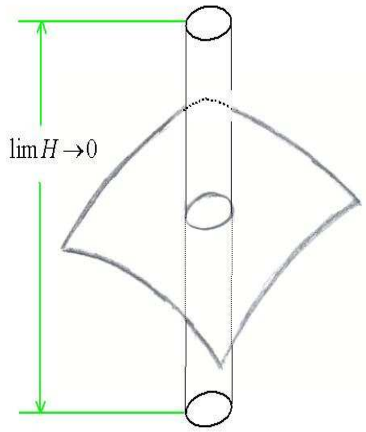

Figure 3: Cylindrical volume to be used to derive jump conditions across a singular surface

5.4 General local equation of balance in Lagrange coordinates

The transition of the local equations of balance from Euler to Lagrange coordinates rely on the definitions

$$\hat{\psi}_v = J\psi_v, \quad \hat{\varphi}_v^k = J\overset{-1}{F}{}^{kj}\varphi_v^j, \quad \hat{\xi}_v = J\xi_v. \tag{52}$$

In regular points, i.e. $X \in V_\pm$, the local version of (45) reads

$$\frac{\partial\hat{\psi}_v}{\partial t} + \frac{\partial\hat{\varphi}_v^k}{\partial X_k} = \hat{\xi}_v. \tag{53}$$

In order to proof the eqn (53) we insert in (50) the definitions $(52)_{1,3}$, and apply the chain rule to the divergence. Due to the identity (13) there appears the quantity $\hat{\varphi}_v^k$ under the divergence.

In order to derive the local analogue of (53) in points of the singular surface $\mathfrak{s}$, we start from (51). Here we insert the definitions $(52)_{1,2}$, then we take care for the identities (39) and (40) and obtain

$$-W_N[[\hat{\psi}_v]] + [[\hat{\varphi}_v^k]]N^k = \sqrt{\frac{g}{G}}\left(-\frac{\partial\psi_s(t, U^\Gamma)}{\partial t} - \psi_s(w^\Delta_{\tau;\Delta} - 2k_M w_\nu) - \varphi^\Delta_{s;\Delta} + \xi_s\right). \tag{54}$$

This is the final form of the generic equation of balance in singular points in Lagrange coordinates. Note that only its left hand side has been transformed from Euler to Lagrange coordinates. In this study it is not necessary to describe also the surface terms on the right hand side of (54) with respect to the reference configuration of the considered body.

5.5 A remark on the equivalence of balance equations in Euler and Lagrange description

The last two sections have revealed a complete equivalence of the generic representation of balance equations in Euler and Lagrange description. Thus at a first glance one might think that it is sufficient to consider only one of the descriptions. However, both are needed, because the special cases, which are related to special physical situations, destroy the equivalence.

For example, if we restrict the velocity of a substance, which crosses the interface, to normal motion, we must decide whether we are interested in normal motion with respect to the actual surface, i.e. $(v^i)^{+/-} = (v_\nu)^{+/-}\nu^i$, or to define normal motion with respect to the reference configuration, i.e. $(v^i)^{+/-} = (v_N)^{+/-}N^i$.

6 The conservation laws for mass, momentum and energy

We are interested exclusively in interfacial boundary condition, i.e. special equations of balance at singular surfaces. For this reason we do not consider the well known special forms of the equations of balance in regular points in detail.

In this chapter we identify the generic densities, fluxes and sources with physical quantities and their properties. In turn the generic equations of balance (51) become physical laws. In particular, the equations of balance become conservation laws if the production densities ξ_v and ξ_s are set equal to zero.

The conservation laws for mass, momentum and energy are the most important ones. They result with special choices for the generic densities, fluxes and productions appearing in (51).

The balance of mass relies on the physical experience that there are neither nonconvective mass fluxes nor mass sources, and we write

$$\begin{aligned} &\psi_v = \rho && \text{bulk mass density,} \\ &\psi_s = \rho_s && \text{surface mass density,} \\ &\varphi_v^k = 0, && \varphi_s^\Delta = 0, \quad \xi_v = 0, \quad \xi_s = 0. \end{aligned} \tag{55}$$

With these settings, the generic jump condition (51) becomes the balance of mass:

$$[[\dot{m}]] = -\frac{\partial \rho_s}{\partial t} - \rho_s(w^\Delta_{\tau;\Delta} - 2k_M w_\nu), \quad \text{with} \quad \dot{m} = \rho(v^k\nu^k - w_\nu). \tag{56}$$

In order to derive the balance of momentum, we ignore external gravitational and Lorentz forces, and in this case physical experience states that there is no source of momentum. We identify

$$\begin{aligned}
\psi_v &= \rho v^i && \text{-bulk momentum density, } v^i \text{ velocity of particles,} \\
\psi_s &= \rho_s w^i && \text{-surface momentum density, } w^i \text{ surface velocity,} && (57)\\
\varphi_v^k &= -\sigma^{ik} && \text{-(Cauchy) stress, force per area,} && (58)\\
\varphi_s^\Delta &= -t_s^{i\Delta} && \text{-surface stress vector} \equiv \text{ force per line,} && (59)\\
\xi_v &= 0, && \xi_s = 0. && (60)
\end{aligned}$$

With these identifications we obtain the momentum balance. Note that we have eliminated two parts on its right hand side by means of the mass balance:

$$[[\dot{m}(v^i - w^i)]] - [[\sigma^{ik}]]\nu^k = -\rho_s \frac{\partial w^i}{\partial t} + t^{i\Delta}_{s;\Delta}. \tag{61}$$

For later use we decompose the surface stress vector into tangential and normal components. We write

$$t_s^{i\Delta} = S^{\Delta\Gamma}\tau^i_\Gamma + S^\Delta \nu^i. \tag{62}$$

The newly introduced quantities $S^{\Delta\Gamma}$ and S^Δ are called surface stress tensor and normal stress, respectively.

Finally we obtain the balance of energy if we identify

$$\begin{aligned}
\psi_v &= \rho(u + \frac{1}{2}v^2) && \text{bulk energy density,} \\
\psi_s &= u_s + \frac{\rho_s}{2}w^2 && \text{surface energy density,} \\
\varphi_v^k &= q^k - \sigma^{ik}v^i && \text{energy flux of the bulk,} && (63)\\
\varphi_s^\Delta &= q_s^\Delta - t_s^{i\Delta}w^i && \text{surface energy flux,} \\
\xi_v &= 0, \quad \xi_s = 0.
\end{aligned}$$

We ignore again external gravitational and Lorentz forces and additionally we ignore energy sources resulting from radiation. In this case physical experience states that there is no further source of energy. The following special form (64) of the energy balance results because again we have eliminated two parts on its right hand side by means of the mass balance:

$$[[\dot{m}(u+\frac{1}{2}v^2-\frac{1}{2}w^2)]]+[[q^k-\sigma^{ik}v^i]]\nu^k = -\rho_s\frac{\partial \frac{1}{2}w^2}{\partial t}-\frac{\partial u_s}{\partial t}-u_s(w^\Delta_{\tau;\Delta}-2k_M w_\nu)-(q_s^\Delta-t_s^{i\Delta}w^i)_{;\Delta}. \tag{64}$$

The decompositions of the energy into internal energy, (ρu, u_s), and kinetic energy, ($\rho/2v^2$, $\rho_s/2w^2$) and of the energy flux into heat flux (q^k, q_s^Δ) and power of stress ($-\sigma^{ik}v^i, -t_s^{i\Delta}w^i$) is induced by the requirement that equations of balance must be invariant with respect to Galileian transformation.

Note that we have not assumed that the internal surface energy is proportional to the surface mass density. It is most important that we do not make this assumption, because it will turn out that even in the case, where inertia of the singular surface is ignored, there still may be a nonzero contribution to the internal surface energy density.

7 Conservation of moment of momentum

Forming the cross product of the momentum balance with the surface position vector $\hat{x}_s^i$ leads to the balance of the moment of momentum, $\rho_s \varepsilon^{ijk} \hat{x}_s^j w^k$, which is in general a nonconserved quantity. The corresponding production ξ_s can be identified with $\varepsilon^{ijk} t_s^{j\Delta} \tau_\Delta^k$, see [27] for more details.

Only if we assume that the surface does not carry any internal moment of momentum, the moment of momentum is a conserved quantity and we have

$$\varepsilon^{ijk} t_s^{j\Delta} \tau_\Delta^k = 0. \tag{65}$$

We introduce here the decomposition (62) of the surface stress vector and conclude

$$S^{\Delta\Gamma} = S^{\Gamma\Delta} \quad \text{and} \quad S^\Delta = 0. \tag{66}$$

This case is well known in the literature, e.g. see [30], and a model, where (66) is satisfied is called *membrane model* in contrast to the *shell model*, where (66) is not satisfied. In physical terms: If a surface, is exposed to mechanical loads and behaves approximately rigid, then $(66)_2$ cannot be valid. Alternatively, if the external load is exclusively balanced by tangential surface stresses, the surface changes its shape, and the restrictions are valid. A rubber membrane provides a prominent example for this case, [8] and [11].

8 Equations of balance for kinetic and internal energy

Multiplying the momentum balance with the surface velocity w^i yields the balance of kinetic energy

$$[[\dot{m}(w^i v^i - w^2)]] - [[\sigma^{ik} w^i]]\nu^k = -\rho_s \frac{\partial w^2/2}{\partial t} + (w^i t_s^{i\Delta})_{;\Delta} - t_s^{i\Delta} \frac{\partial w^i}{\partial U^\Delta}. \tag{67}$$

We subtract now the balance of kinetic energy from the balance of (total) energy (64) and obtain the balance of internal energy

$$\begin{aligned} &[[\dot{m}(u + \frac{1}{2}(v - w)^2)]] + [[q^k]]\nu^k - [[\sigma^{ik}(v^i - w^i)]]\nu^k = \\ &= -\frac{\partial u_s}{\partial t} - u_s(w^\Delta_{\tau;\Delta} - 2k_M w_\nu) - q^\Delta_{s;\Delta} + t_s^{i\Delta} \frac{\partial w^i}{\partial U^\Delta}. \end{aligned} \tag{68}$$

The Stefan condition and its generalizations will turn out as special cases of the balance of internal energy.

9 Equations of balance for the partial masses

Next we form balance equations for the partial masses. These read

$$[[\dot{m}(c_a - c_{sa})]] + [[J_a^k]]\nu^k = -\rho_s \frac{\partial c_{sa}}{\partial t} - J^{\Delta}_{s;\Delta} + \zeta_{sa}. \tag{69}$$

The balance of partial mass (69) follows from the general equation of balance (51) if we identify

$\psi_v = \rho c_a$ partial bulk mass density, c_a concentration of constituent a,
$\psi_s = \rho_s c_{sa}$ partial surface mass density, c_{sa} surface concentration of constituent a,
$\varphi_v^k = J_a^k = \rho c_a(v_a^k - v^k)$, diffusion flux, v_a^k velocity of constituent a (70)

$$\text{with } \sum_{a=1}^{a_c} J_a^k = 0,$$

$$\varphi_s^{\Delta} = J_{sa}^{\Delta}, \quad \text{surface diffusion flux} \quad \text{with } \sum_{a=1}^{a_c} J_{sa}^{\Delta} = 0, \tag{71}$$

$$\xi_v = \zeta_{va}, \quad \text{production rate of constituent a} \quad \text{with } \sum_{a=1}^{a_c} \zeta_a = 0,$$

$$\xi_s = \zeta_{sa}, \quad \text{surface production rate of constituent a} \quad \text{with } \sum_{a=1}^{a_c} \zeta_{sa} = 0.$$

In order to obtain the balance equations (69), we have again eliminated two parts on the right hand side of (51) by means of the mass balance.

The partial masses are nonconserved quantities, neither in the bulk nor on a singular surface, because chemical reactions might take place. However, the total mass is conserved, and this fact implies the given restrictions for the diffusion fluxes and the productions rates, respectively.

10 Equations of Balance for the entropy

Another important quantity is the entropy, which is nonconserved in nonequilibrium processes. The equation of balance for the entropy at singular surfaces reads

$$[[\dot{m}s]] + [[\varphi^k]]\nu^k = -\frac{\partial s_s}{\partial t} - s_s(w^{\Delta}_{\tau;\Delta} - 2k_M w_\nu) - (\varphi_s^{\Delta})_{;\Delta} + \varsigma_s. \tag{72}$$

The balance of the entropy (72) follows from the general equation of balance (51) if we identify

$$\begin{array}{ll} \psi_v = \rho s & \text{bulk entropy density,} \quad s \text{ specific entropy,} \\ \psi_s = s & \text{surface entropy density,} \\ \varphi_v^k = \phi^k & \text{(nonconvective) entropy flux in the bulk,} \\ \varphi_s^\Delta = \phi_s^\Delta & \text{surface entropy flux,} \\ \xi_v = \varsigma_v & \text{local bulk entropy production with} \quad \varsigma_v \geq 0, \\ \xi_s = \varsigma_s & \text{local surface entropy production with} \quad \varsigma_s \geq 0. \end{array} \tag{73}$$

We ignore entropy sources due to radiation. Physical experience states that the local entropy production rates are nonnegative. We call this statement the *strong second law of thermodynamics*, because this law goes beyond the famous statement that was proved by Rudolf Clausius, [7], [27]: The temporal change of the total entropy, S, of a body, whose outer surface is at uniform temperature T cannot be smaller but the ratio of heat supply $\dot{Q}$ divided by T:

$$\frac{dS}{dt} \geq \frac{\dot{Q}}{T}. \tag{74}$$

Note that, similarly to the surface energy density, we have not assumed that the surface entropy density is proportional to the surface mass density. It is most important that we do not make this assumption, because it will turn out that even in the case, where inertia of the singular surface is ignored, there is a nonzero contribution to the surface entropy density.

11 A simplified interfacial model

If we ignore singular lines on $\mathfrak{s}$, the given singular equations of balance for mass, momentum, internal energy, partial masses and entropy represent the most general case. Dariadtion, external gravitational forces and Lorentz forces are represented by volume denistives, and thus exclusively enter the regular equations of balance but not their singular counterparts.

Now we will introduce some simplifications which bring the singular equations of balance in a simpler form. The following choices of simplifications are made with the objective to present illustrative examples which yield (i) well known jump conditions at interfacial boundaries and the underlying assumptions, (ii) generalizations regarding mechanical effects and jump conditions where ordered solids and vacancies are involved.

The most general case that we will study from now on relies on the restrictions

$$
\begin{aligned}
\rho_s = 0, &\quad \text{and} \quad c_{sa} = 0, \quad \text{no interfacial inertia,} \\
J^{\Delta}_{sa} = 0, &\quad \text{no tangential diffusion flux at the interface,} \\
q^{\Delta}_{sa} = 0, &\quad \text{no tangential heat flux at the interface,} \\
\phi^{\Delta}_{sa} = 0, &\quad \text{no tangential entropy flux at the interface,} \\
[[T]] = 0, &\quad \text{the temperature is continuous across the interface.}
\end{aligned}
\tag{75}
$$

Note that chemical production and entropy production within the interface are still allowed.

Interfacial chemical reactions are described by ζ_{sa}, which gives the interfacial mass production rate of constituent a. We assume that N_R different chemical reactions might happen within the interface, and these are indexed by $r \in \{1, 2, ..., N_R\}$. The stoichiometric coefficient of constituent a in the reaction r is denoted by γ^r_a. Let Γ^r be the net rate of reaction r, so that the mass production rate can the be written

$$
\zeta_{sa} = \sum_{r=1}^{N_R} \gamma^r_a M_a \Gamma^r, \tag{76}
$$

where M_a demotes the molecular weight of constituent a.

Finally we summarize the general singular balance equations according to the given restrictions. There follows the balance of mass, balance of momentum, balance of internal energy, balance of partial masses and the balance of entropy, respectively:

$$
\begin{aligned}
&[[\dot{m}]] = 0, \quad \text{with} \quad \dot{m} = \rho(v^k \nu^k - w_\nu) \\
&\dot{m}[[v^i]] - [[\sigma^{ik}]]\nu^k = (S^{\Delta\Gamma}_{;\Delta} - S^{\Delta} b^{\Gamma}_{\Delta})\tau^i_\Gamma + (S^{\Delta\Gamma} b_{\Delta\Gamma} + S^{\Delta}_{;\Delta})\nu^i \\
&\dot{m}[[(u + \frac{1}{2}(v - w)^2)]] + [[q^k]]\nu^k - [[\sigma^{ik}(v^i - w^i)]]\nu^k = \\
&-\frac{\partial u_s}{\partial t} - u_s(w^{\Delta}_{\tau;\Delta} - 2k_M w_\nu) + S^{\Delta\Gamma}(g_{\Gamma\Sigma} w^{\Sigma}_{\tau;\Delta} - b_{\Delta\Gamma} w_\nu) + S^{\Delta}(\frac{\partial w_\upsilon}{\partial U^{\Delta}} + w^{\Sigma}_{\tau} b_{\Sigma\Delta}) \\
&\dot{m}[[c_a]] + [[J^k_a]]\nu^k = \sum_{r=1}^{N_R} \gamma^r_a M_a \Gamma^r \\
&\dot{m}[[s]] + \frac{1}{T}[[(q^k - \sum_{a=1}^{a_c} \mu_a J^k_a)]]\nu^k = -\frac{\partial s_s}{\partial t} - s_s(w^{\Delta}_{\tau;\Delta} - 2k_M w_\nu) + \varsigma_s \quad \text{with} \quad \varsigma_s \geq 0.
\end{aligned}
\tag{77}
$$

The mass balance now implies the continuity of the mass flux $\dot{m}$ through the interface. Thus we may remove $\dot{m}$ out of the jump brackets in the other balance equations.

12 The second law of thermodynamics for singular surfaces

In this section we derive the Gibbs equation for surfaces. In general its derivation is cumbersome, but follows the strategy that is carefully described by I. Müller in the monograph [27]. For that reason we start here from the simplied surface model of the last section.

We multiply the entropy balance $(77)_5$ by the temperature T , which is continuous in the simplied case, and subtract the result from the internal energy balance $(77)_4$.

There follows

$$-T\varsigma_s = -\frac{\partial\psi_s}{\partial t} - s_s\frac{\partial T}{\partial t} + (S^{\Delta\Gamma} - \psi_s g^{\Delta\Gamma})(g_{\Gamma\Sigma}w^{\Sigma}_{\tau;\Delta} - b_{\Delta\Gamma}w_\nu) + S^\Delta(\frac{\partial w_\upsilon}{\partial U^\Delta} + w^{\Sigma}_{\tau}b_{\Sigma\Delta})$$
$$+\dot{m}[[(\psi + \frac{1}{2}(\upsilon - w)^2)]] - [[\sigma^{ik}(\upsilon^i - w^i)]]\nu^k + [[\sum_{a=1}^{a_c}\mu_a J^k_a]]\nu^k \leq 0. \tag{78}$$

Herein we have introduced the specific free energy of the bulk $\psi = u - Ts$ and the surface free energy density $\psi_s = u_s - Ts_s$ with the physical units $Joule/kg$ and $Joule/m^2$, respectively. We recall from Section 2 that by definition $\psi_s \equiv \sigma$, where σ is called surface tension, which is sometimes a misleading designation.

We assume now that the surface free energy density, the surface entropy density and the surface stress depend at most on the set

$$T, \frac{\partial T}{\partial U^\Delta}, g_{\Delta\Gamma}, g^0_{\Delta\Gamma}, b_{\Delta\Gamma}, b^0_{\Delta\Gamma}, \nu^i, \nu^{0i}. \tag{79}$$

The quantities $g^0_{\Delta\Gamma}, b^0_{\Delta\Gamma}, \nu^{0i}$ are metric tensor, curvature tensor and normal vector, respectively, at the reference time $t = 0$, so that the pairs $(g_{\Delta\Gamma}, g^0_{\Delta\Gamma})$, $(b_{\Delta\Gamma}, b^0_{\Delta\Gamma})$, (ν^i, ν^{0i}) are measures of the deformation of the surface. See [8] and [11], where the deformation of a rubber balloon may serve as an illustrative example.

After carrying out the necessary differentiations in (78), we observe that the surface entropy production depends linearly on

$$\frac{\partial T}{\partial t}, \frac{\partial^2 T}{\partial U^\Delta \partial t}, w^{\Sigma}_{\tau;\Delta}, \frac{\partial w_\upsilon}{\partial U^\Delta}, \frac{\partial b_{\Delta\Gamma}}{\partial t}. \tag{80}$$

However, the inequality must hold for arbitrary values of these fields, and thus we conclude that the factors of the derivatives (80) must vanish, because otherwise we could violate the inequality. This statement is discussed at length for various circumstances and materials in [27]. The consequences are:
(i) surface free energy density, surface entropy density, surface stress and normal stress do not depend on

$$\frac{\partial T}{\partial U^\Delta} \quad \text{and} \quad b_{\Delta\Gamma}, \tag{81}$$

(ii) there holds the Gibbs equation for surfaces, which may be written as

$$s_s = -\frac{\partial\sigma}{\partial T}, \quad S^{\Delta\Gamma} = \sigma g^{\Delta\Gamma} + \frac{1}{2}\frac{\partial\sigma}{\partial g_{\Delta\Gamma}}, \quad S^{\Delta} = -g^{\Delta\Gamma}\tau^k_\Gamma\frac{\partial\sigma}{\partial\nu^k}, \tag{82}$$

(iii) there remains the inequality

$$-T\varsigma_s = \dot{m}[[(\psi + \frac{1}{2}(\upsilon - w)^2)]] - [[\sigma^{ik}(\upsilon^i - w^i)]]\nu^k + [[\sum_{a=1}^{a_c}\mu_a J^k_a]]\nu^k \leq 0, \tag{83}$$

which will be further exploited in Section 15.

13 Mechanical equilibrium

13.1 Equilibrium conditions

Mechanical equilibrium is established if the barycentric velocity υ^i is zero. On the other hand, impermeable interfaces are defined by $(\upsilon^k)^{+/-}\nu^k = w_\nu$ so that there is no (total) mass flux across the interface. Note that impermeable interfaces may still allow a flux of partial masses.

Both cases lead to the same mechanical equilibrium conditions, which follow from $(77)_2$ and can

$$-[[\sigma^{ik}]]\nu^i\nu^k = S^{\Delta\Gamma}b_{\Delta\Gamma} + S^{\Delta}_{;\Delta} \quad \text{and} \quad -[[\sigma^{ik}]]\tau^i_\Sigma\nu^k = g_{\Gamma\Sigma}(S^{\Delta\Gamma}_{;\Delta} - S^{\Delta}b^{\Gamma}_{\Delta}). \tag{84}$$

We conclude from the constitutive laws $(83)_{1,2}$ and the conditions (84) for mechanical equilibrium that the jump $[[\sigma^{ik}]]\nu^i\nu^k$ of the Cauchy stress can be calculated if the surface free energy density is known. The determination of the jump $-[[\sigma^{ik}]]\tau^i_\Sigma\nu^k$ needs additional information on the antisymmetric part $S^{[\Delta\Gamma]}$ of the surface stress $S^{\Delta\Gamma}$. However, it turns out that this jump is of minor importance, in particular it is not needed to determine the jumps of the chemical potentials, see Sections 15.3 and 15.4 for more details.

We consider two interesting special cases. (i) If the bulk materials are mixtures of nonviscous fluids, their stress is represented by a pressure, $\sigma^{ik} = -p\delta^{ik}$. If furthermore the surface free energy is a function of temperature only, $\sigma(T)$, the equilibrium conditions reduce to

$$[[p]] = 2\sigma k_M \quad \text{and} \quad \frac{\partial\sigma}{\partial T}\frac{\partial T}{\partial U^\Delta} = 0. \tag{85}$$

We conclude that the pressure jump is proportional to the mean curvature of the interface, see Section 2. This law was first derived by Laplace for spheres, [23]. In addition, the temperature must be uniform on the interface.

(ii) Now we assume that the surface tension depends exclusively on the normal vector, $\sigma(\nu^i)$, which itself is a function of the surface parameters U^Δ. Let us introduce the function $\hat{\sigma}(t, U^\Delta) = \sigma(\nu^i(t, U^\Delta))$, and by means of the identity

$$\frac{\partial \hat{\sigma}}{\partial U^\Delta} = -b^\Gamma_\Delta \tau^k_\Gamma \frac{\partial \sigma}{\partial \nu^k}, \tag{86}$$

we may rewrite the conditions (85) according to

$$-[[\sigma^{ik}]]\nu^i\nu^k = 2\hat{\sigma}k_M + (\overset{-1}{b})^{\Delta\Gamma}\hat{\sigma}_{;\Delta\Gamma} + (\overset{-1}{b})^{\Delta\Gamma}_{;\Delta}\hat{\sigma}_{;\Gamma} \quad \text{and} \quad -[[\sigma^{ik}]]\tau^i_\Sigma\nu^k = g_{\Sigma\Gamma}S^{[\Delta\Gamma]}_{;\Delta}. \tag{87}$$

13.2 Discussion and comparison with the literature

In 1950 C. Herring introduced a surface free energy density that depends on the interfacial normal vector in order to study sintering processes where small particles decrease their free energy by growing together, [19]. In the same article Herring also considered interfacial elasticity and he showed that the surface stress tensor should be calculated according to the relation $(82)_2$, which follows here as a consequence of the second law of thermodynamics.

In 1972 and 1974 J.W. Cahn & D.W. Hoffmann put forward the studies on anisotropy of interfaces, [20], [21]. They ignored interfacial elasticity and considered the case where the interfacial free energy density σ exclusively depends on the interfacial normal vector ν^i. Cahn and Hoffmann substituted σ by the capillarity vector ξ^i, which nowadays is called Hoffmann/Cahn vector, and they equipped ξ^i with the properties

$$\sigma = \xi^i\nu^i, \quad d\sigma = \xi^i d\nu^i, \quad \nu^i d\xi^i = 0. \tag{88}$$

In [21] Cahn and Hoffmann established the equilibrium law

$$[[p]] = div_s \cdot \xi. \tag{89}$$

In our notation the operator $div_s\cdot$ reads

$$div_s \cdot \xi = g^{\Gamma\Delta}\tau^i_\Delta \frac{\partial \xi^i}{\partial \nu^i}, \tag{90}$$

While the explicit meaning of $div_s\cdot$ is not generally given in [21], it appears explicitly in Garcke/Nestler/Stoth, [14], where a sharp interface limit of a phase field model is carried out.

We now compare our results with the Cahn/Hoffmann law (89). To this end we start from (84) and assume according to Cahn/Hoffmann that σ exclusively depends on ν^i. There follows with (88)

$$-[[\sigma^{ik}]]\nu^i\nu^k = 2\sigma k_M - g^{\Gamma\Delta}\tau^i_\Delta\left(\frac{\partial \xi^k\nu^k}{\partial \nu^i}\right)_{;\Delta} = -div_s \cdot \xi, \tag{91}$$

which gives the Cahn/Hoffmann law (89) if the bulk stress fields are isotropic.

The tangential components of $[[\sigma^{ik}]]\nu^k$ are related to the antisymmetric part of the surface stress tensor, $S^{[\Gamma\Sigma]}$, because there results

$$[[\sigma^{ik}]]\tau^i_\Delta \nu^k = g_{\Delta\Gamma} S^{[\Gamma\Sigma]}_{;\Sigma}. \tag{92}$$

Next we calculate the surface stress vector $t^{i\Delta}$, which gives the force per line element of the interface. We introduce the surface vector

$$X^i_\Gamma = \epsilon^{ijk}\tau^j_\Gamma \nu^k, \tag{93}$$

which lies in the tangential plane and is perpendicular to the direction Γ. We obtain

$$t^{i\Delta} = \epsilon^{ijk}\xi^j X^k_\Gamma g^{\Gamma\Delta}. \tag{94}$$

This is the Hoffmann/Cahn representation of the surface stress vector, which is best suited to study triple junctions.

Note that both the Cahn/Hoffmann relations (89) and (94) only hold if interfacial elasticity is ignored and if temperature is uniform on the interface.

In the literature the Hoffmann/Cahn framework is used to compare the sharp interface limit of phase field models with pure sharp interface models and to relate the higher gradient coefficients of phase field models with the surface free energy density σ. Various examples are found to be in McFadden & Wheeler [38] , Nestler & Wheeler [31], Garcke, Nestler & Stoth [14], Dreyer & Wagner [12].

Interfacial elastic effects have also already been considered by other authors. Alexander & Johnson calculated jump conditions for disordered solid/liquid interfaces including interfacial elasticity via the minimization of the Gibbs free energy [2]. Gurtin & Voorhees propose balance equations to derive jump conditions with elastic effects, and they give a systematic evaluation of the second law of thermodynamics, [17] and [18]. However, their reasonings rely on the so called configurational forces, which are not needed in the current study, where we exclusively deal with the classical forces of mechanics.

14 The Stefan condition and its generalizations

In this section we discuss the assumptions that lead to the well known Stefan condition

$$-w_\nu\lambda + [[q^k]]\nu^k = 0. \tag{95}$$

The quantity λ may depend on temperature and is called latent heat in the literature, [25].

The Stefan condition must obviously result as a special case of the internal energy balance $(77)_3$, and we will now analyse the necessary assumptions. To this end let us at first assume (i) $\sigma^{ik} = -p\delta^{ik}$, and (ii) $v^i = 0$, (iii) $\psi_s = \sigma(T)$, (iv) $w^i = w_\nu\nu^i$ so that the energy balance $(77)_3$ can be reduced to

$$-w_\nu\rho[[(u + \frac{p}{\rho} + \frac{1}{2}w^2]] + [[q^k]]\nu^k = T\frac{\partial^2\sigma}{\partial T^2}\frac{\partial T}{\partial t} - T\frac{\partial\sigma}{\partial T}2k_M w_\nu. \tag{96}$$

In case that we neglect the kinetic energy of the interface, we may identify the latent heat as $\lambda = \rho[[(u+\frac{p}{\rho}]]$, which is in accordance to classical thermodynamics. However, even now the Stefan condition does not result. The first contribution on the right hand side of (96) only vanishes either in processes with constant temperature, or if the surface entropy density does not depend on T. However, this is an exceptional case. But even then, there is a second contribution which is proportional to the mean curvature and to the interfacial normal speed. Finally, it is important to note that the surface parameters must be chosen so that (iv) is satisfied. See [12], where an example is given that a different choice is often prefered due to numerical aspects.

15 Interfacial equilibrium conditions and growth laws

15.1 On the general structure of the interfacial entropy production

The physical law whereupon the interfacial entropy production is positive in irreversible processes and zero in equilibrium gives rise to further important jump conditions involving the chemical potentials at the interface. The derivation of these conditions relies on the interfacial entropy inequality (83). In the next section we will show that the interfacial entropy inequality can be brought into a sum of binary products:

$$-T\varsigma_s = \sum_{A=1}^{N} F_A D_A \leq 0. \tag{97}$$

The quantities D_A and F_A are called driving forces and fluxes, respectively, see also Abeyratne and Knowles [1] for a very interesting example.

Driving forces that result from sharp interface limits of phase field models a derived and discussed in [5], [6], and [12].

In equilibrium the interfacial entropy production is zero and always positive in nonequilibrium processes. If the interfacial processes do produce interfacial entropy, we exploit the inequality (97) as follows, see also Gurtin & Voorhees, [17] and Liu [24]: We assume that there are constitutive laws that relate the driving forces $D_1, D_2, ..D_N$ to the interfacial fluxes F_A as $F_A = \tilde{F}_A(D_B, W)$, where W abbreviates other variables that are not among the driving forces. We conclude from (97) that ς_s assumes a minimum for $D_A = 0$, and furthermore we have

$$(\frac{\partial}{\partial D_B}(\sum_{A=1}^{N} \tilde{F}_A D_A))_{|equ.} = \tilde{F}_{B|equ.} = 0, \quad B \in \{1, 2, .., N\}. \tag{98}$$

In other words

$$D_B = 0 \Leftrightarrow F_B = 0 \quad \text{in equilibrium.} \tag{99}$$

Thus it follows that the fluxes can be represented by

$$F_A = -\sum_{B=1}^{N} M_{AB} D_B \quad \text{with} \quad M_{AB} \quad \text{– positive definite.} \tag{100}$$

The matrix M_{AB} contains the surface mobilities of the interface, which must be determined experimentally. However, they also can be calculated from an underlying kinetic theory. Section 2 provides an example for the latter case. The constitutive law (100) is called *growth law.*

There exist an interesting limiting case. We recall that $D_A = 0$ implies $F_A = 0$. However, if the surface mobilities are much larger than the bulk mobilities, we may consider the limit $M_{AB} \to \infty$, and then we must have $D_B = 0$, so that the fluxes F_A remain finite. In this case, the equilibrium conditions $D_A = 0$ still holds, but the fluxes F_A will be calculated from interfacial balance equations, and the process under consideration is called *diffusion controlled.*

On the other hand, if the interface mobilities are comparable or smaller as the bulk mobilities, the considered process relies on the law (100) and is called *interface controlled.*

Next we identify the driving forces and fluxes explicitly.

15.2 Alternative representation of the interfacial entropy inequality

The exploitation of the interfacial entropy production (83) yields simple results only if we consider the two special cases: (i) either the bulk materials consist of isotropic fluids or (ii) the bulk materials move at the interface exclusively in normal direction, i.e.

$$\text{in case (i):} \quad \sigma^{ik} = -p\delta^{ik} \quad \text{or in case (ii):} \quad \upsilon^i = \upsilon_\nu \nu^i. \tag{101}$$

In both cases, the inequality (83) reduces to

$$-T\varsigma_s = \dot{m}[[(\psi + \frac{1}{2}(\upsilon - w)^2)\delta^{ik} - \frac{1}{\rho}\sigma^{ik}]]\nu^i\nu^k + [[\sum_{a=1}^{a_c} \mu_a J_a^k]]\nu^k \le 0. \tag{102}$$

From now on we consider exclusively the special case (ii).

For a further simplification of the inequality (102), we define the quantity

$$\dot{m}_a^{+/-} = (\dot{m}c_a + J_a^k \nu^k)^{+/-}, \tag{103}$$

which gives the total one sided flux of constituent a across the interface. The singular mass balance $(77)_5$ can now be written

$$[[\dot{m}_a]] = \sum_{r=1}^{N_R} M_a \gamma_a^r \Gamma^r, \tag{104}$$

and there holds due to $(71)_3$

$$\sum_{a=1}^{a_c^{+/-}} \dot{m}_a^{+/-} = \dot{m}. \tag{105}$$

Next we eliminate the diffusion flux in the inequality (102) and take care for the Gibbs/Duhem equation (21) to obtain

$$-T\varsigma_s = \dot{m}[[\frac{1}{2}(v-w)^2 - \frac{1}{\rho}\sigma^{<ik>}\nu^i\nu^k]] + [[\sum_{a=1}^{a_c}\dot{m}_a\mu_a]] \leq 0. \tag{106}$$

For a further exploitation of this form of the entropy inequality we need to know the behaviour of the various constituents at the interface. In general there are four different kinds of constituents, and we put them into four groups as follows. The first group contains constituents that may cross the interface without being subjected to chemical reactions, i.e.

$$\Lambda_1 = \{a\,|\,\dot{m}_a^+ = \dot{m}_a^-, \dot{m}_a^\pm \neq 0\}. \tag{107}$$

The members of the second group of constituents cannot cross the interface, because they experience the interface as an impermeable wall, i.e.

$$\Lambda_2 = \{a\,|\,\dot{m}_a^+ = 0,\ \dot{m}_a^- = 0\}. \tag{108}$$

The third group contains constituents appearing on both sides at the interface, and they are involved in interfacial chemical reactions, i.e.

$$\Lambda_3 = \{a\,|\,\dot{m}_a^+ - \dot{m}_a^- = \sum_{r=1}^{N_R} M_a\gamma_a^r\Gamma^r\}. \tag{109}$$

Finally there is a fourth group $\Lambda_4 = \Lambda_4^+ \cup \Lambda_4^-$ of constituents that are also involved in interfacial chemical reactions but they appear either on the "+" side or on the "-" side of the interface, i.e.

$$\Lambda_4^{+/-} = \{a\,|\,\dot{m}_a^{+/-} = (+/-)\sum_{r=1}^{N_R} M_a\gamma_a^r\Gamma^r\}. \tag{110}$$

We proceed to rewrite the inequality (106) and in particular the second jump bracket, which now can be written

$$\begin{aligned}[[\sum_{a=1}^{a_c}\dot{m}_a\mu_a]] = \sum_{a\in\Lambda_1}\dot{m}_a[[\mu_a]] + \sum_{a\in\Lambda_3} < \dot{m}_a > [[\mu_a]] + \sum_{r=1}^{N_R}\Gamma^r\sum_{a\in\Lambda_3} M_a\gamma_a^r < \mu_a > + \\ \sum_{r=1}^{N_R}\Gamma^r(\sum_{a\in\Lambda_4^+} M_a\gamma_a^r\mu_a^+ + \sum_{a\in\Lambda_4^-} M_a\gamma_a^r\mu_a^-)\ .\end{aligned} \tag{111}$$

Next we assume that the constituent $a = 1$ belongs to Λ_1, and we eliminate $\dot{m}_1$ by means of the side condition (106). The final result reads

$$
\begin{aligned}
-T\varsigma_s = {} & \dot{m}[[(\mu_1 + \frac{1}{2}(v-w)^2) - \frac{1}{\rho}\sigma^{<ik>}\nu^i\nu^k]] + \\
& \sum_{a\in\Lambda_1} \dot{m}_a[[\mu_a - \mu_1]] + \sum_{a\in\Lambda_3} < \dot{m}_a > [[\mu_a - \mu_1]] + \\
& \sum_{r=1}^{N_R} \Gamma^r \Big(\sum_{a\in\Lambda_3} M_a\gamma_a^r < \mu_a > + \sum_{a\in\Lambda_4^+} M_a\gamma_a^r(\mu_a^+ - \frac{1}{2}[[\mu_1]]) + \sum_{a\in\Lambda_4^-} M_a\gamma_a^r(\mu_a^- + \frac{1}{2}[[\mu_1]]) \, .
\end{aligned}
\tag{112}
$$

Note that the representations (106) and (112) of the interfacial entropy production are equivalent. However, the representation (112) will be only applied to identify driving forces and fluxes for the special case that (i) the solid phase is a *disordered solid*, i.e. there are no privileged lattice sites, and (ii) no vacancies appear.

The other interesting case is: (i) the solid has a sublattice structure, so that privileged lattice sites can be described, and (ii) vacancies are taken into account. This case will be treated on the basis of the representation (106).

15.3 Identification of fluxes and driving forces for disordered solids without vacancies

In this section we consider interfaces between two fluids, between fluids and disordered solids without vacancies, and between two disordered solid phases without vacancies, respectively. In these cases and unlike when ordered solids are involved, the only side condition is given by (105). Thus we may directly identify the fluxes and driving forces in the inequality (112) by its comparison with the general inequality (97). We read off the fluxes

$$
F_A = \Big\{ \dot{m}, \dot{m}_{a\in\Lambda_1}, < \dot{m}_{a\in\Lambda_3} >, \dot{m}^+_{a\in\Lambda_4^+}, \dot{m}^-_{a\in\Lambda_4^-}, \Gamma^{r\in\{1,2\ldots,N_R\}} \Big\} ,
\tag{113}
$$

and the corresponding driving forces

$$
\begin{aligned}
D_A = \{ & [[(\mu_1 + \frac{1}{2}(v-w)^2) - \frac{1}{\rho}\sigma^{<ik>}\nu^i\nu^k]], [[\mu_a - \mu_1]]_{a\in\Lambda_1}, [[\mu_a - \mu_1]]_{a\in\Lambda_3}, \\
& (\sum_{a\in\Lambda_3} M_a\gamma_a^r < \mu_a > + \sum_{a\in\Lambda_4^+} M_a\gamma_a^r(\mu_a^+ - \frac{1}{2}[[\mu_1]]) + \sum_{a\in\Lambda_4^-} M_a\gamma_a^r(\mu_a^- + \frac{1}{2}[[\mu_1]]))_{r\in\{1,2\ldots,N_R\}} \} .
\end{aligned}
\tag{114}
$$

15.3.1 Evolution to equilibrium, growth laws

If all the interfacial processes happen without entropy productions, and if N constituents are able to cross the interface, there follow $N + N_R$ conditions for the interfacial values of concentrations and stresses:

$$\begin{aligned}
&[[\mu_1 + \frac{1}{2}(v-w)^2)]] = [[\frac{1}{\rho}\sigma^{<ik>}]]\nu^i\nu^k \\
&[[\mu_a - \mu_1]] = 0 \quad \text{for} \quad a \in \Lambda_1 \cup \Lambda_3,\, a = 1 \in \Lambda_1, \\
&(\sum_{a\in\Lambda_3} M_a\gamma_a^r < \mu_a > + \sum_{a\in\Lambda_4^+} M_a\gamma_a^r(\mu_a^+ - \frac{1}{2}[[\mu_1]]) + \\
&\sum_{a\in\Lambda_4^-} M_a\gamma_a^r(\mu_a^- + \frac{1}{2}[[\mu_1]])_{r\in\{1,2\dots,N_R\}} = 0 \quad \text{for} \quad r \in \{1,2,\dots N_R\}
\end{aligned} \tag{115}$$

Recall that these interfacial equilibrium conditions hold if either no interfacial entropy production appears or if all the surface mobilities are large, so that we may consider the limit $M_{AB} \to \infty$. In this case we must set $D_B = 0$ to obtain finite fluxes F_A, and the fluxes will be calculated from the interfacial balance equations. Recall that we have called such process *diffusion controlled*.

Obviously, we also may meet situations where the various surface mobilities are of different order. For example, it may happen that chemical reactions establish equilibrium much faster as the two other processes. In this case we have

$$\begin{aligned}
&(\sum_{a\in\Lambda_3} M_a\gamma_a^r < \mu_a > + \sum_{a\in\Lambda_4^+} M_a\gamma_a^r(\mu_a^+ - \frac{1}{2}[[\mu_1]]) + \\
&\sum_{a\in\Lambda_4^-} M_a\gamma_a^r(\mu_a^- + \frac{1}{2}[[\mu_1]])_{r\in\{1,2\dots,N_R\}} = 0 \quad \text{for} \quad r \in \{1,2,\dots N_R\} \quad \text{and} \\
&F_A = -\sum_{B=1}^{N} M_{AB} D_B \quad \text{for} \quad A, B \in \{1,2,\dots N\}.
\end{aligned} \tag{116}$$

15.3.2 Examples for interfacial equilibrium conditions

In this section we assume that all considered processes are diffusion controlled so that the driving forces are zero. The following examples serve for an illustration of the resulting conditions.

Single substance The interface separates two different phases, which both consist of a single substance. In this case we have $c_1 = 1$ and the chemical potential μ_1 becomes the specific Gibbs free energy, g. Correspondingly, there follows only a single condition from (115), which read

$$[[\mu_1 + \frac{1}{2}(v-w)^2)]] = [[\frac{1}{\rho}\sigma^{<ik>}]]\nu^i\nu^k \quad \text{with} \quad \mu_1 = g = \psi - \frac{1}{3\rho}\sigma^{kk}. \tag{117}$$

If we neglect the kinetic energy and if the substance is mechanically described by an isotropic stress, i.e. $\sigma^{ik} = -p\delta^{ik}$, there follows the classical result

$$[[g]] = 0 \quad \text{with} \quad g = \psi + \frac{p}{\rho}. \tag{118}$$

In Section 2 we have already recognized the jump condition (118) as the base for the classical Gibbs/Thomson law. We conclude now that the Gibbs/Thomson law only holds in fluids, because in general we have $\sigma^{<ik>} \neq 0$ in solids.

Binary mixture Now let us consider an interface that separates two phases consisting of binary mixtures. We assume additionally that both constituents may cross the interface without chemical reactions. From (115) we read off the two conditions

$$[[\mu_1 + \frac{1}{2}(v-w)^2]] = [[\frac{1}{\rho}\sigma^{<ik>}]]\nu^i\nu^k \quad \text{and} \quad -[[\mu_1]] + [[\mu_2]] = 0. \tag{119}$$

Thus only if we neglect the kinetic energy and assume again an isotropic stress, we obtain the known result

$$[[\mu_1]] = [[\mu_2]] = 0. \tag{120}$$

Solid/liquid interface with five constituents In this example we consider a solid/liquid interface, $(+/-)$. There are three constituents, A, B, C, in the solid and four constituents, A, B, D, E, in the liquid. The constituents A, B are found to be in both phases, while C, D, E cannot cross the interface. Furthermore we assume that within the interface there is a chemical reaction between the constituents C and D, i.e.

$$\gamma_C C_+ + \gamma_D D_- = 0. \tag{121}$$

For example, if oxygen appears in the liquid as the molecule O_2, it dissociates into $2O$ within the interface before it can occupy a lattice site of the solid.

Thus we read off from eqn. (115) three conditions, viz.

$$\begin{aligned} &[[\mu_A + \frac{1}{2}(v-w)^2]] = [[\frac{1}{\rho}\sigma^{<ik>}]]\nu^i\nu^k, \\ &[[\mu_A]] - [[\mu_B]] = 0, \\ &\gamma_C M_C \mu_C^- + \gamma_D M_D \mu_D^+ = 0. \end{aligned} \tag{122}$$

Furthermore there are three special flux conditions, viz.

$$(J_C^k)^- = -\dot{m}c_C^-, \quad (J_D^k)^- = -\dot{m}c_D^-, \quad (J_E^k)^- = -\dot{m}c_E^-. \tag{123}$$

This example may also serve to illustrate that a sufficient number of conditions are available to determine all unknowns at the interface. To this end we simplify the considered process, by assuming (i) mechanical and interfacial chemical equilibrium is established, (ii) the temperature is uniform and constant, (iii) the barycentric velocity, v^i, vanishes, and (iv) the bulk fluxes are given by Ficks law

$$J_a^k = -\sum_{b=1}^{a_c} m_{ab} \frac{\partial(\mu_b - \mu_1)}{\partial x^k}. \tag{124}$$

Let us further assume that the mechanical problem, that we discussed above have already been solved. Then there remain eight unknowns at the interface, viz. seven concentrations, $c_A^+, c_A^-, c_B^+, c_B^-, c_C^-, c_D^-, c_E^-$, and the normal speed, w_ν, of the interface. For its determination we thus need eight equations. The first six equations are already be given by the conditions (122) and (123), and there are two further jump conditions for the constituents A and B that may cross the interface, viz.

$$-\rho w_\nu(c_A^+ - c_A^-) + ((J_A^k)^+ - (J_A^k)^-)\nu^k = 0, \quad -\rho w_\nu(c_B^+ - c_B^-) + ((J_B^k)^+ - (J_B^k)^-)\nu^k = 0. \tag{125}$$

15.4 Identification of driving forces and fluxes for ordered solids and with vacancies

15.4.1 Statement of the problem: Solid/liquid interfaces in semiinsulating Gallium Arsenide

In this section we consider the interface between a liquid and an ordered solid with sublattice structure and vacancies. Interfaces in semi-insulating Gallium Arsenide (GaAs) will serve as an important example, where the distinctions to the previous case with disordered solids can at best be illustrated.

Single crystal GaAs contains the major elements gallium and arsenic, and additionally various trace elements, which are of most importance in order to fabricate semiconducting or semi-insulating GaAs, respectively. All constituents occupy three sublattices of face-centered cubic (fcc) symmetry. The sublattices are indicated by three Greek letters: α, β, γ. The lattice α is dominantly occupied by gallium, while the arsenic is the major substance on the lattice sites of sublattice β. The sublattice γ indicates an interstitial lattice, where the dominant elements are vacancies. For a proper application of single crystal semi-conducting or semi-insulating GaAs as a wafer material, it is crucial that the trace elements are distributed homogeneously on the lattice sites of the three sublattices. In order to remove dislocations, which appear during the process of crystal growth, a special heat treatment of the wafer becomes necessary. However, the heat treatment might start a diffusion process, where the trace elements move preferably towards the vicinity of the dislocations and find here thermodynamic conditions so that the formation of liquid droplets, dominantly formed by the arsenic, sets in. The complete thermodynamic model that takes care for 16 constituents is described in [36], [37], [9], [10].

Here we consider a simplified case with a solid/liquid interface. The three sublattices of the solid are occupied by gallium (Ga), arsenic (As) and vacancies (V). We assume that Ga is only found on sublattice α, while the other constituents can be found on all three sublattices. Thus there are seven constituents in the solid, viz.

$$Ga_\alpha, As_\alpha, As_\beta, As_\gamma, V_\alpha, V_\beta, V_\gamma. \tag{126}$$

and Ga_L, As_L in the liquid, so that Ga and As can cross the interface while the vacancies are created or annihilated here.

We are confronted here with two new problems: (i) There are several side conditions due to the fact that all three sublattices have the same number densities, n_{SL}, of sublattice sites. (ii) The creation or annihilation of vacancies at the interface is obviously not accompanied by creation or annihilation of mass.

15.4.2 Interfacial entropy inequality for ordered solid/liquid interfaces

The two mentioned problems require a change of the thermodynamic description by a transition from the one sided mass fluxes to one sided mole fluxes. There holds

$$\dot{m}_a^{+/-} = (\dot{m}c_a + J_a^k \nu^k)^{+/-} = M_a \dot{n}_a^{+/-} = M_a(\dot{n}y_a + j_a^k \nu^k)^{+/-} \quad \text{with} \quad \dot{m} = \sum_{a=1}^{a_c^{+/-}} M_a \dot{n}_a^{+/-}. \tag{127}$$

The newly introduced quantities are: M_a - molecular weight, $\dot{n}$ - total mole flux, $\dot{n}_a^{+/-}$ - one sided mole flux, y_a -mole fraction, j_a^k - mole diffusion flux.

Next we re-scale the chemical potentials according to $\tilde{\mu}_a = M_a \mu_a$. The unit of the chemical potential has thus been changed from *Joule/kg* to *Joule/mole*. We consider vacancies as massless particles, ie. we set $M_{V_\alpha} = M_{V_\beta} = M_{V_\gamma} = 0$, however, nevertheless they are carrier of energy and entropy. For this reason we introduce the following rule: The rescaled chemical potentials $\tilde{\mu}_{V_\alpha}$, $\tilde{\mu}_{V_\beta}$, $\tilde{\mu}_{V_\gamma}$ of the vacancies are nonzero.

The general interfacial entropy inequality (102) can thus be written

$$-T\varsigma_s = \sum_{a=1}^{a_c^{+/-}} M_a \dot{n}_a^{+/-} [[\frac{1}{2}(v-w)^2 - \frac{1}{\rho}\sigma^{<ik>}\nu^i\nu^k]] + [[\sum_{a=1}^{a_c} \dot{n}_a \tilde{\mu}_a]] \leq 0. \tag{128}$$

We assume that the $+/-$ refers to solid and liquid, respectively, and we write in detail

$$\begin{aligned}-T\varsigma_s = {} & (M_{Ga}\dot{n}_{Ga_\alpha} + M_{As}(\dot{n}_{As_\alpha} + \dot{n}_{As_\beta} + \dot{n}_{As_\gamma}))[[\frac{1}{2}(v-w)^2 - \frac{1}{\rho}\sigma^{<ik>}\nu^i\nu^k]] + \\ & \dot{n}_{Ga_\alpha}\tilde{\mu}_{Ga_\alpha} - \dot{n}_{Ga_L}\tilde{\mu}_{Ga_L} + \dot{n}_{As_\alpha}\tilde{\mu}_{As_\alpha} + \dot{n}_{As_\beta}\tilde{\mu}_{As_\beta} + \dot{n}_{As_\gamma}\tilde{\mu}_{As_\gamma} - \dot{n}_{As_L}\tilde{\mu}_{As_L} + \\ & \dot{n}_{V_\alpha}\tilde{\mu}_{V_\alpha} + \dot{n}_{V_\beta}\tilde{\mu}_{V_\beta} + \dot{n}_{V_\gamma}\tilde{\mu}_{V_\gamma} \leq 0.\end{aligned} \tag{129}$$

There are four additional side conditions:

(i) Conservation of mass

$$\dot{n}_{Ga_\alpha} = \dot{n}_{Ga_L}, \quad \dot{n}_{As_\alpha} + \dot{n}_{As_\beta} + \dot{n}_{As_\gamma} = \dot{n}_{As_L}. \tag{130}$$

(ii) Equal number densities of lattice sites

$$\dot{n}_{Ga_\alpha} + \dot{n}_{As_\alpha} + \dot{n}_{V_\alpha} = \dot{n}_{As_\beta} + \dot{n}_{V_\beta} = \dot{n}_{As_\gamma} + \dot{n}_{V_\gamma}. \tag{131}$$

These conditions serve to eliminate four one sided fluxes in the interfacial entropy inequality. We chose $\dot{n}_{Ga_L}$, $\dot{n}_{As_L}$, $\dot{n}_{V_\alpha}$, $\dot{n}_{V_\gamma}$, and obtain

$$\begin{aligned}
-T\varsigma_s = \dot{n}_{Ga_\alpha}(\tilde{\mu}_{Ga_\alpha} - \tilde{\mu}_{Ga_L} - \tilde{\mu}_{V_\alpha} + [[\frac{M_{Ga}}{2}(\upsilon - w)^2 - \frac{M_{Ga}}{\rho}\sigma^{<ik>}\nu^i\nu^k]])+ \\
\dot{n}_{As_\alpha}(\tilde{\mu}_{As_\alpha} - \tilde{\mu}_{As_L} - \tilde{\mu}_{V_\alpha} + [[\frac{M_{As}}{2}(\upsilon - w)^2 - \frac{M_{As}}{\rho}\sigma^{<ik>}\nu^i\nu^k]])+ \\
\dot{n}_{As_\beta}(\tilde{\mu}_{As_\beta} - \tilde{\mu}_{As_L} + \tilde{\mu}_{V_\alpha} + \tilde{\mu}_{V_\gamma} + [[\frac{M_{As}}{2}(\upsilon - w)^2 - \frac{M_{As}}{\rho}\sigma^{<ik>}\nu^i\nu^k]])+ \\
\dot{n}_{As_\gamma}(\tilde{\mu}_{As_\gamma} - \dot{n}_{As_L}\tilde{\mu}_{As_L} - \tilde{\mu}_{V_\gamma} + [[\frac{M_{As}}{2}(\upsilon - w)^2 - \frac{M_{As}}{\rho}\sigma^{<ik>}\nu^i\nu^k]])+ \\
\dot{n}_{V_\beta}(\tilde{\mu}_{V_\alpha} + \tilde{\mu}_{V_\beta} + \tilde{\mu}_{V_\gamma}) \leq 0.
\end{aligned} \tag{132}$$

15.4.3 Identification of fluxes and driving forces

We compare the interfacial entropy inequality ((132)) with the general form (97) to identify five fluxes

$$F_A = \{\dot{n}_{Ga_\alpha}, \dot{n}_{As_\alpha}, \dot{n}_{As_\beta}, \dot{n}_{As_\gamma}, \dot{n}_{V_\beta}\} \tag{133}$$

and five driving forces

$$\begin{aligned}
D_A = \{\tilde{\mu}_{Ga_\alpha} - \tilde{\mu}_{Ga_L} - \tilde{\mu}_{V_\alpha} + [[\frac{M_{Ga}}{2}(\upsilon - w)^2 - \frac{M_{Ga}}{\rho}\sigma^{<ik>}\nu^i\nu^k]], \\
\dot{n}_{As_\alpha}(\tilde{\mu}_{As_\alpha} - \tilde{\mu}_{As_L} - \tilde{\mu}_{V_\alpha} + [[\frac{M_{As}}{2}(\upsilon - w)^2 - \frac{M_{As}}{\rho}\sigma^{<ik>}\nu^i\nu^k]], \\
\dot{n}_{As_\beta}(\tilde{\mu}_{As_\beta} - \tilde{\mu}_{As_L} + \tilde{\mu}_{V_\alpha} + \tilde{\mu}_{V_\gamma} + [[\frac{M_{As}}{2}(\upsilon - w)^2 - \frac{M_{As}}{\rho}\sigma^{<ik>}\nu^i\nu^k]], \\
\tilde{\mu}_{As_\gamma} - \dot{n}_{As_L}\tilde{\mu}_{As_L} - \tilde{\mu}_{V_\gamma} + [[\frac{M_{As}}{2}(\upsilon - w)^2 - \frac{M_{As}}{\rho}\sigma^{<ik>}\nu^i\nu^k]], \\
\tilde{\mu}_{V_\alpha} + \tilde{\mu}_{V_\beta} + \tilde{\mu}_{V_\gamma}\}.
\end{aligned} \tag{134}$$

15.4.4 Interfacial equilibrium conditions for solid/liquid interfaces in GaAs

In this section we assume that all considered processes are diffusion controlled, so that the driving forces are zero. We neglect as usual the kinetic energy, and in this case the resulting conditions read

$$
\begin{aligned}
&\tilde{\mu}_{Ga_\alpha} - \tilde{\mu}_{Ga_L} - \tilde{\mu}_{V_\alpha} = [[\frac{M_{Ga}}{\rho}\sigma^{<ik>}\nu^i\nu^k]],\\
&\tilde{\mu}_{As_\alpha} - \tilde{\mu}_{As_L} - \tilde{\mu}_{V_\alpha} = [[\frac{M_{As}}{\rho}\sigma^{<ik>}\nu^i\nu^k]],\\
&\tilde{\mu}_{As_\beta} - \tilde{\mu}_{As_L} + \tilde{\mu}_{V_\alpha} + \tilde{\mu}_{V_\gamma} = [[\frac{M_{As}}{\rho}\sigma^{<ik>}\nu^i\nu^k]],\\
&\tilde{\mu}_{As_\gamma} - \tilde{\mu}_{As_L} - \tilde{\mu}_{V_\gamma} = [[\frac{M_{As}}{\rho}\sigma^{<ik>}\nu^i\nu^k]],\\
&\tilde{\mu}_{V_\alpha} + \tilde{\mu}_{V_\beta} + \tilde{\mu}_{V_\gamma} = 0.
\end{aligned}
\tag{135}
$$

These five conditions together with the four side conditions (130) and (131) yield nine algebraic equations, that may be used to determine the nine interfacial number densities of the constituents if the mechanical part of the problem has been solved.

In case that the bulk phases are homogeneous and in equilibrium, there exist an alternative method to derive the jump conditions (135). This method relies on the exploitation of the statement, that for given and fixed values of temperature and external load, equilibrium in a two phase mixture is established by the minimum of the available free energy. This approach is carried out for the *GaAs* problem without mechanical phenomena by Wenzl, Mika, Henkel, [36], and Wenzl, Oates, Mika, [36], and with mechanical/chemical coupling by Dreyer, Duderstadt [9], [10].

In either case, the jump conditions (135) that apply when ordered solids are involved, cannot be obtained as a special case from the jump conditions (115), which give the classical textbook results for interfacial conditions. We have shown here that the latter only hold in disordered mixtures, a fact which is not mentioned in many textbooks.

16 Local equations of balance in Lagrange coordinates

16.1 Equations of balance for partial masses, momentum, energy and entropy

The special jump conditions (77), which are formulated by means of Euler coordinates, will now form the base for a derivation of the corresponding jump conditions in Lagrange coordinates.

We start with the relations $(77)_1$, (39), (40) involving normal vectors and interfacial normal speeds in Euler and Lagrange coordinates:

$$\dot{m} = -\rho J\sqrt{\frac{G}{g}}W_N, \quad \text{with} \quad [[\dot{m}]] = 0, \quad \nu^i = \sqrt{\frac{G}{g}}J\overset{-1}{F^{ki}}N^k, \quad w^i = \upsilon^i_{+/-} + F^{ij}_{+/-}W^j. \tag{136}$$

We conclude from $(136)_1$ and $(136)_3$ that the products ρJ and $J\overset{-1}{F^{ki}}N^k$ are continuous across the interface:

$$[[\rho J]] = 0, \quad [[J\overset{-1}{F^{ki}}]]N^k = 0. \tag{137}$$

Recall that we consider as before exclusively the case, where the barycentric velocity is restricted to normal motion, i.e. $\upsilon^i = \upsilon_\nu \nu^i$ at the interface. Furthermore we restrict the surface parameters so that a surface point moves exclusively in normal direction, i.e. we set $w^i = w_\nu \nu^i$. In this case, the eqn. $(136)_4$ implies $\tau^i_\Delta F^{ij}W^j = 0$.

Finally we recall the definitions (52), and define accordingly

$$\rho_0 = \rho J, \quad \rho_{0a} = \rho_a J, \quad \hat{J}^k_a = J\overset{-1}{F^{ki}}J^i_a, \quad \hat{q}^k = J\overset{-1}{F^{ki}}q^i. \tag{138}$$

We insert these relations and definitions into the jump conditions (77). There follow the corresponding jump conditions in Lagrange coordinates:

$$\begin{aligned}
&-\rho_0 W_N[[\upsilon^i]] - [[\hat{\sigma}_{ik}]]N^k = \sqrt{\frac{g}{G}}((S^{\Delta\Gamma}_{;\Delta} - S^\Delta b^\Gamma_\Delta)\tau^i_\Gamma + (S^{\Delta\Gamma}b_{\Delta\Gamma} + S^\Delta_{;\Delta})\nu^i) \\
&-\rho_0 W_N[[(u + \frac{1}{2}W_N^2 F^{ij}F^{ij})\delta^{ks} - \frac{1}{\rho_0}\hat{\sigma}^{ik}F^{is}]]N^k N^s + [[\hat{q}^k]]\nu^k = \\
&\sqrt{\frac{g}{G}}(-\frac{\partial u_s}{\partial t} - u_s(w^\Delta_{\tau;\Delta} - 2k_M w_\nu) + S^{\Delta\Gamma}(g_{\Gamma\Sigma}w^\Sigma_{\tau;\Delta} - b_{\Delta\Gamma}w_\nu) + S^\Delta(\frac{\partial w_\upsilon}{\partial U^\Delta} + w^\Sigma_\tau b_{\Sigma\Delta}))
\end{aligned} \tag{139}$$

$$\begin{aligned}
&-\rho_0 W_N[[c_a]] + [[\hat{J}^k_a]]N^k = \sqrt{\frac{g}{G}}\sum_{r=1}^{N_R}\gamma^r_a M_a \Gamma^r \\
&-\rho_0 W_N[[s]] + [[\frac{1}{T}(\hat{q}^k - \sum_{a=1}^{a_S}\mu_a \hat{J}^k_a)]]N^k = \sqrt{\frac{g}{G}}(-\frac{\partial s_s}{\partial t} - s_s(w^\Delta_{\tau;\Delta} - 2k_M w_\nu) + \varsigma_s) \\
&\qquad\qquad \text{with} \quad \varsigma_s \geq 0.
\end{aligned}$$

Note that the write hand sides of the eqn. (139) are not transformed into Lagrange coordinates.

The form of the kinetic energy in the internal energy balance $(139)_3$ results as follows:

$$\begin{aligned}
[[\frac{1}{2}(\upsilon - W)^2]] &= [[\frac{1}{2}F^{ij}F^{ik}]]W^j W^k = [[\frac{1}{2}F^{ij}F^{ik}]]N^j N^k W_N^2 = \\
&= < F^{ij} > [[F^{ik}]]N^j N^k W_N^2 = \frac{1}{2}[[W_N^2 F^{ij}F^{ij}]],
\end{aligned} \tag{140}$$

where the last equality relies on the Hadamard condition $(30)_2$, which implies

$$< F^{ij} > [[F^{ik}]]N^j N^k = < F^{ij} > [[F^{ij}]]. \tag{141}$$

16.2 Interfacial entropy production

In this section we derive the interfacial entropy production corresponding to its counterpart in Euler coordinates. As before we consider exclusively the special case where the temperature is continuous across the interface, $[[T]] = 0$. We multiply the interfacial entropy balance $(139)_4$ by T, and subtract the resulting equation from the balance of internal energy $(139)_4$. There follows the interfacial entropy production in Lagrange coordinates

$$-\rho_0 W_N[[(\psi+\frac{1}{2}W_N^2 F^{ij}F^{ij})\delta^{ks}-\frac{1}{\rho_0}\hat{\sigma}^{ik}F^{is}]]N^k N^s+[[\sum_{a=1}^{a_S}\mu_a \hat{J}_a^k)]]N^k = \sqrt{\frac{g}{G}}(-T\varsigma_s) \leq 0. \tag{142}$$

The quantity $\psi\delta^{ks} - \frac{1}{\rho_0}\hat{\sigma}^{ik}F^{is}$ is known as the Eshelby tensor in the mechanical literature. Eshelby has introduced this tensor in [13], see also Liu [24] and Mura [29] for further examples that illustrate the role of the Eshelby tensor.

In order to obtain from (142) useful equilibrium conditions and growth laws, we have at first to specialize the second bracket involving chemical potentials and diffusion fluxes. However, this procedure can be done according to the same strategy that we have developed in Section 15, and will not carried out here.

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