Mathematical Modeling of Batteries based on Balance Equations and Coupled Thermo-Electrodynamics

with a thermodynamic consistent derivation of porous electrode theory

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Für meine Eltern

“Thermodynamik ist ein komisches Fach. Das erste Mal, wenn man sich damit befasst, versteht man nichts davon. Beim zweiten Durcharbeiten denkt man, man hätte nun alles verstanden, mit Ausnahme von ein oder zwei kleinen Details. Das dritte Mal, wenn man den Stoff durcharbeitet, bemerkt man, dass man fast gar nichts davon versteht, aber man hat sich inzwischen so daran gewöhnt, dass es einen nicht mehr stört.”

Arnold Sommerfeld [1]

Contents

List of Publications

Within the scope of this thesis the following publications originated:

- K. Becker-Steinberger, S. Funken, M. Landstorfer and K. Urban, "A Mathematical Model for All Solid- State Lithium-Ion Batteries", *ECS Trans.*, 2010, **25**, 285–296.
- M. Landstorfer, S. Funken and T. Jacob, "An advanced model framework for solid electrolyte intercalation batteries", *Phys. Chem. Chem. Phys.*, 2011, **13**, 12817–12825.
- M. Landstorfer and T. Jacob, "Mathematical modeling of intercalation batteries at the cell level and beyond", *Chem. Soc. Rev.*, 2013, **42**, 3234–3252.

Abstract

This work covers a revision of balance equations in moving geometries. Based on general transport theorems, local equations of balance for volumes and surfaces are generally derived. This set of equations is then used to derive a coupled thermo-electrodynamic field theory, with local mass, momentum and energy densities. A mixture theory is then employed, based on a local second law, for the description of liquid and solid electrolytes (and thus also for intercalation electrodes). The application of this model framework is straight forward applied to model a lithium ion battery on the cell level. Porous electrode theory with a consistent reaction boundary condition is finally stated and compared to standard modeling approaches.

Overview and Summary

Mathematical modeling of lithium ion batteries is a key feature for a profound understanding of the whole spectrum of phenomena occurring in such electrochemical systems. Due to their inherent multiscale nature, batteries cannot be described with a single equation. Contrary, it is necessary to fully understand the whole framework of coupled thermo- and electrodynamics in order to derive consistent theoretical models in terms of partial differential equations. In this sense, I carefully revise the derivation of field equations in thermo-electrodynamics based on general balance equations.

Local field equations are essentially obtained from a generalization of the Leibniz integral rule, *i.e.* the prescription of exchanging a (parametric) derivative and a (volumetric) integration. Chapter 1 covers the derivation of the Leibniz integral rule for volumes as well as embedded surfaces and curves in $\mathbb{R}^3$. Applying this concept in the $\mathbb{R}^3$ with an additional parameter $t \in I$, a step wise derivation of the general Reynold transport theorem for time dependent volumes $\Omega(t)$, surfaces $\Sigma(t) \in \mathbb{R}^3$ and curves $\Psi(t) \in \mathbb{R}^3$ is given. From a variational principle the local partial differential equation for scalar and vectorial properties in the volume $\Omega(t)$ and on the surface $\Sigma(t)$ are obtained. General coordinate transformations between different Eulerian descriptions of a time dependent domain are further investigated, leading to transformation laws of the local PDEs.

In chapter 2, the concept of density functions, *i.e.* the integral description of macroscopic properties such as mass M or momentum $\vec{p}$, is employed to derive local balance equations for a mixture of n different species. With a derivation of Maxwells equations, based on balance equations of flux properties, the momentum and energy of the electromagnetic field are *derived*. It is then shown that neither energy nor momentum of the field is conserved, as well as the momentum and kinetic energy of mass. Due to a local version of Newtons second law, *i.e.* conservation of total momentum, the general Lorentz force (in a field theoretical sense) for polarize and magnetizeable materials is derived. Similar, a local version of the first law of thermodynamics introduces the internal energy density ρu and states the conservation of total energy. The actual sink of kinetic- and electromagnetic energy arises as source of internal energy.

Thermodynamics arises then with the introduction of an entropy function ρs, coupling all the independent field variables. The second law of thermodynamics is then stated in the form of a balance equation for ρs, with a non-negative source term r_s, *i.e.* the entropy production. With a similar formulation of the local second law for embedded surfaces, one obtains the continuity condition of the chemical potential as well as the Young–Laplace equation. The explicit exploitation of the local second law (*i.e.* the entropy principle) leads to necessary conditions of the mass and heat flux, regarding their dependency on the thermodynamic driving forces. Variable changes and transformations lead then to the concept of the free energy, *i.e.* the Helmholtz free energy $\rho\psi$ and the Gibbs free energy g,

in a field theoretical sense. The concept of material functions is consequently introduced, stating an explicit representation of the physical property g in terms of the unknown field variables, *e.g.* $g = \mathfrak{g}(T, p, c_1, \ldots, c_{\mathrm{n}-1})$. Sketching the concept of Pfaffian forms and integrability conditions, explicit material functions are further derived. The entropy function is essentially obtained from two concepts of *counting* particles, *i.e.* the configurational entropy in free space and on a lattice. Additional contributions to the material due to pressure and temperature are briefly stated, leading finally to complete material functions for an incompressible liquid electrolyte mixture as well as a solid electrolyte mixture (with constant lattice). Note that these concepts cover also materials in which only uncharged species are present.

Chapter 3 uses the framework derived in Chapter 2 for a thermodynamic consistent modeling of an intercalation battery. After briefly sketching the setup of a common lithium ion cell, separate models for the electrolyte and the electrode phase are developed. The electrolyte is essentially modeled as an ideal, incompressible mixture. Generalized Poisson–Nernst–Planck equations are then derived and compared to classical results. Assuming further a strong electroneutrality condition leads to a generalized ohmic law for the cations in the electrolyte phase, as well as a balance equations for the anions and a corresponding heat equation.
Modeling of the porous electrode phase is hierarchically built up, starting from a single particle model via a discrete many particle model finally leading to a porous electrode theory. In the single particle model, the general balance equations for intercalated lithium on a lattice structure are stated. Various material functions are briefly discussed, including ideal and regular mixtures on a lattice, as well as phase boundary contributions. Based on equilibrium conditions for all thermodynamic driving forces, the open circuit potential of a cell is derived. With a regular solution model the open circuit potential of a two particle electrode is investigated. It shows a homogenized phase separation, *i.e.* within each particle the phases are homogenous, however, different from particle to particle. This effect was also found to be the origin of hysteresis[2] in $LiFePO_4$ based batteries. Stepping further to a many particle model, porous electrode theory is motivated due to the huge amount of single particles in a realistic battery electrode.
Averaging techniques are employed to derive homogenized balance equations of the mixed electrode/electrolyte phase from the equation framework. The porous electrolyte phase is then described with an averaged electrochemical potential of charge and an averaged anion density as well as an averaged temperature. Based on the strong electroneutrality assumption, a macroscopic ohmic law is derived, with a (macroscopic) volumetric source/sink term covering the electrochemical intercalation reaction. The porous electrode, however, is described with a multiscale variable $\hat{\theta}(\mathbf{x}, r, t)$, where the micro scale covers the amount of intercalated lithium within a particle and the macro scale its actual position in space. Based on a single electrode model, *i.e.* an ideal solution on a lattice, a multiscale transport equation is derived, which covers the intercalation reaction as flux boundary condition. A comparison to classically used models (*i.e.* the Newman model [3]) regarding the open circuit potential is then briefly performed. It is shown that the Newman model actually relays on a doubtable material model for the (microscopic) electrode particle. This circumstance is understood as *cause* of the thermodynamic inconsistent prediction[1] of the open circuit potential in porous electrode theory.
Finally, a thermodynamic consistent reaction rate model for the intercalation reaction is stated. Dependent on the respective *thermodynamic ansatz* function (to ensure the local

[1] Actually an additional parameter is introduced in the model, fitted to experimental data, to correct this circumstance.

second law), either the Tafel- or the Buttler–Voler equation is obtained. The transition of a Buttler–Voler-equation for porous electrodes is finally sketched, with a consistent incorporation of the open circuit potential.

In summary, the work is to be understood as a very *basis* of a thermodynamic consistent modeling procedure to address a variety of questions arising in battery cell chemistry.

1

Mathematical basics, transport theorems and balance equations

In this chapter the mathematical basics are derived which are required to formulate a coupled thermodynamic and electrodynamic field theory in chapter 2. It consist mainly of the derivation of transport theorems, the formulation of balance equations and coordinate transformations.

1.1 Transport theorems

The local equations of continuum mechanics, in general partial differential equations (PDEs), are essentially obtained from global integral equations and the condition that these global equations hold for each and every subset of the desired domain. Transport theorems are used to exchange time derivatives and spatial integration, leading to expressions like

$$\int\limits_{\Omega(t)} h_V(f(\mathbf{x},t), \partial_t f(\mathbf{x},t), \nabla f(\mathbf{x},t), \dots)\, dV = 0. \tag{1.1}$$

Clearly, if this equation holds for arbitrary $\omega \subset \Omega(t)$ one deduces via a variational principle the local equation

$$h_V(f(\mathbf{x},t), \partial_t f(\mathbf{x},t), \nabla f(\mathbf{x},t), \dots) = 0. \tag{1.2}$$

Such local equations for scalar and vector fields in volumes, on surfaces and on curves will gradually be derived in this section, following the hierarchy given in figure 1.1 and 1.2.

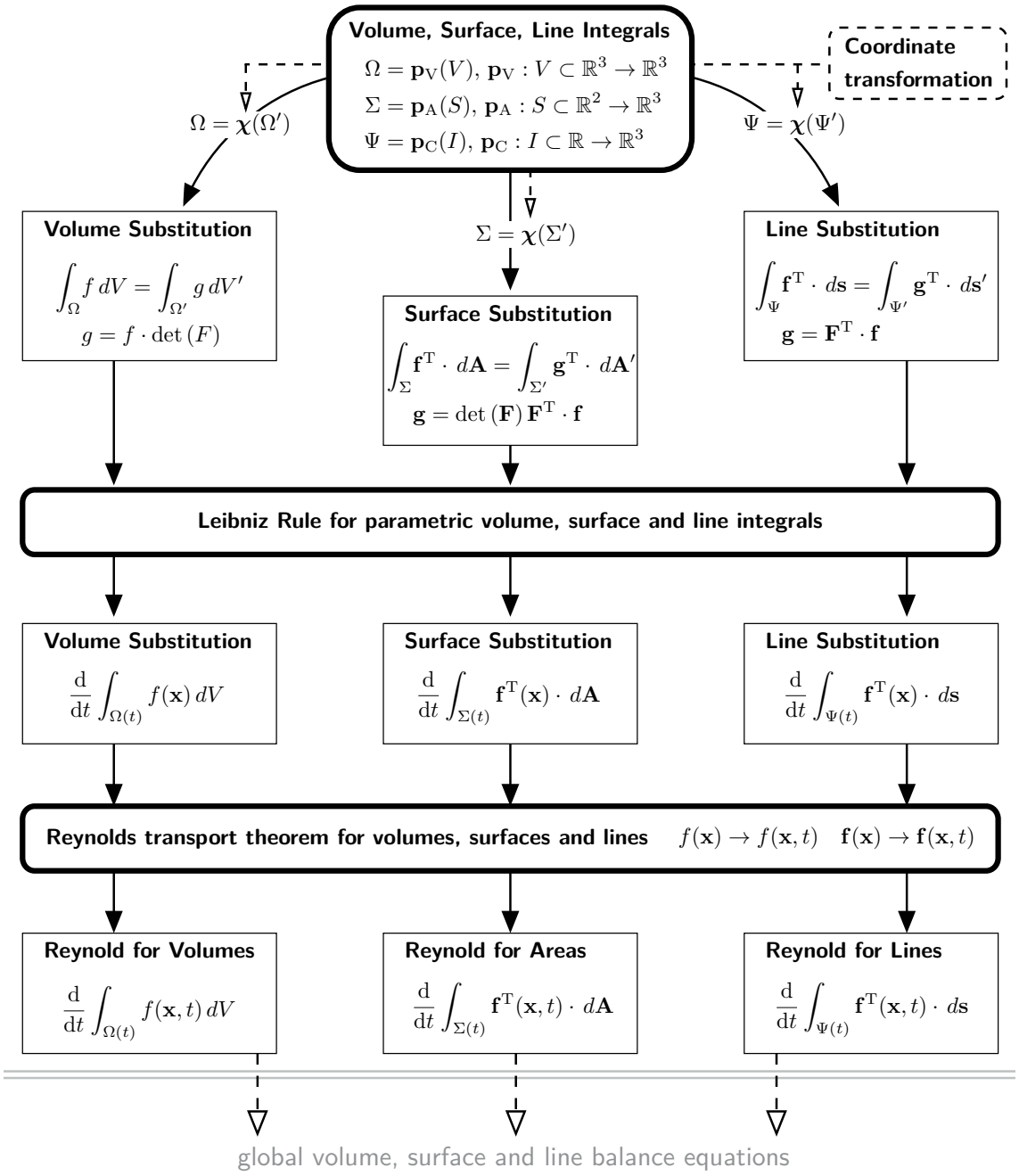

Figure 1.1.: Schematic overview and hierarchy of the derivation of Reynold's transport theorem for volumes, surfaces and curves. The diffeomorphism $\boldsymbol{\chi} : \mathbb{R}^3 \supset \Omega' \to \Omega \subset \mathbb{R}^3$ is the mapping function from the initial domain Ω' to the Eulerian domain $\Omega(t)$.

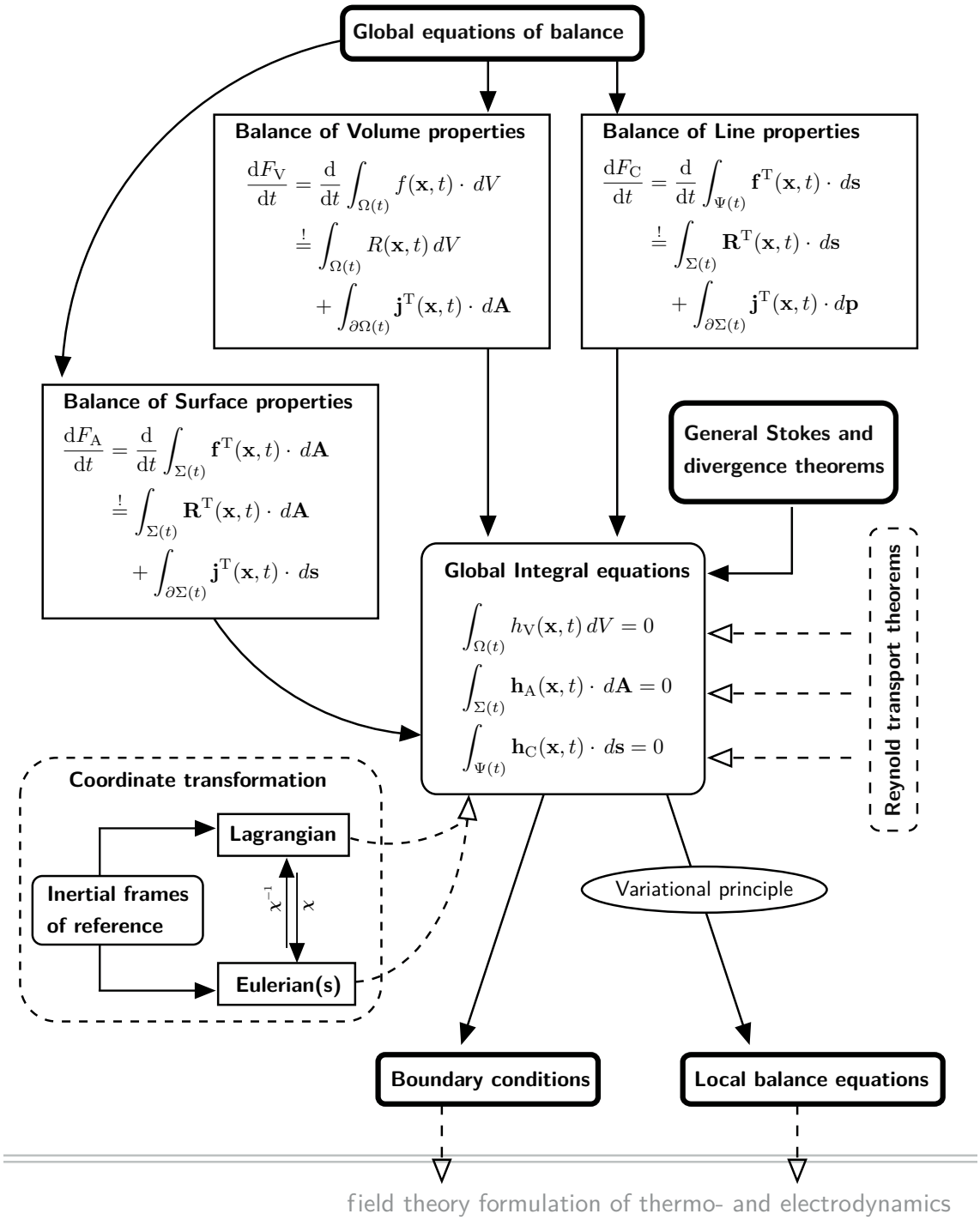

Figure 1.2.: Schematic overview and hierarchy of the derivation of the local PDEs from global balance or conservation equations. Coordinate transformations ensure the formulation of the resulting PDEs in different frames of reference.

1.1.1 Integral transformations

At the very beginning in the derivation of transport theorems are integral transformations on surfaces, volumes and curves. Usually, surface and line integral transformations are performed with a diffeomorphism mapping the parametric domain of the desired surface or curve to another one. Here, however, the diffeomorphism maps the embedded surface in $\mathbb{R}^3$ onto another one in $\mathbb{R}^3$ (and similar for curves). Identifying the vector gradient (or jacobian) of some general diffeomorphism as linear operator on the respective tangent space allows generalization of linear transformation theorems. Based on this, parametric domains can be mapped onto some reference or fixed domain which allows then an exchange of integration and the parametric derivative. This leads to generalizations of the Leibniz integral theorem for volumes, surfaces and curves, and finally to Reynolds transport theorem for termed manifolds. The order

- surface integrals
- volume integrals
- curve integrals

is due to the emphasis on surface transformations and its deviation from *classical* surface integral transformations.

The transformation laws are derived via some descriptive examples on transformations of parallelograms and parallelepipeds under linear transformations. These are then generalized to transformations of arbitrary surfaces and volumes under linear transformations, and finally studied for general diffeomorphisms.

Surface integrals

Let a parallelogram Σ be spanned by $\mathbf{a}$ and $\mathbf{b}$ and the offset $\mathbf{x}_0$, *i.e.* the graph of parallelogram is given by

$$\mathbf{p}_A(u,v) = \mathbf{x}_0 + u\mathbf{a} + v\mathbf{b} \quad (u,v) \in S = [0,1]^2. \tag{1.3}$$

Then $\Sigma = \mathbf{p}_A(S) \in \mathbb{R}^3$ and the area of Σ is calculated via

$$\begin{aligned}
\text{area}\{\Sigma\} &= \int_\Sigma dA = \iint_S \left\| \frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v} \right\| d(u,v) && (1.4)\\
&= \iint_S ||\mathbf{a} \times \mathbf{b}||\, d(u,v) && (1.5)\\
&= ||\mathbf{a} \times \mathbf{b}||\,. && (1.6)
\end{aligned}$$

Since Σ is a surface embedded in $\mathbb{R}^3$, two kinds of surface integrals arise, either for scalar functions $f(\mathbf{x})$, $\mathbf{x} \in \Sigma$ or vector fields $\mathbf{f}(\mathbf{x})$.

Definition 1 (Surface integral of the first and second kind)**.**

Let a surface Σ in the three dimensional space be parametrized by some graph $\mathbf{p}_A(u,v)$, $(u,v) \in S = [0,1]^2$ and assume $\Sigma = \mathbf{p}_A(S)$ is a regular surface (*i.e.* $\frac{\partial \mathbf{p}_A}{\partial u}$ and $\frac{\partial \mathbf{p}_A}{\partial v}$ are linear independent). The **surface integral of the first kind** of a function $f(\mathbf{x})$, $\mathbf{x} \in \Sigma$ is then

defined as

$$\int_{\Sigma} f(\mathbf{x})\, dA(\mathbf{x}) := \iint_{S} f(\mathbf{p}_A(u,v)) \left|\left| \frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v} \right|\right| d(u,v). \tag{1.7}$$

For a vector field $\mathbf{f}(\mathbf{x}) \in \mathscr{C}^{\infty}(\mathbb{R}^n)$, $\mathbf{x} \in \Sigma$ the **surface integral of the second kind** is defined as

$$\int_{\Sigma} \mathbf{f}^{\mathrm{T}}(\mathbf{x}) \cdot\, d\mathbf{A}(\mathbf{x}) := \iint_{S} \mathbf{f}^{\mathrm{T}}(\mathbf{p}_A(u,v)) \cdot \left(\frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v} \right) d(u,v) \tag{1.8}$$

$$= \iint_{S} \mathbf{f}^{\mathrm{T}}(\mathbf{p}_A(u,v)) \cdot \underbrace{\frac{\frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v}}{\left|\left| \frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v} \right|\right|}}_{=:\mathbf{n}(\mathbf{p}_A(u,v))} \left|\left| \frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v} \right|\right| d(u,v) \tag{1.9}$$

$$= \int_{\Sigma} \mathbf{f}^{\mathrm{T}}(\mathbf{x}) \cdot \mathbf{n}(\mathbf{x})\, dA(\mathbf{x}). \tag{1.10}$$

Sometimes the equivalent typeface

$$\int_{\Sigma} \mathbf{f}^{\mathrm{T}}(\mathbf{x}) \cdot\, d\mathbf{A}(\mathbf{x}) = \int_{\Sigma} \langle \mathbf{f}(\mathbf{x}),\, d\mathbf{A}(\mathbf{x}) \rangle = \int_{\Sigma} \langle \mathbf{f}(\mathbf{x}), \mathbf{n}(\mathbf{x}) \rangle\, dA(\mathbf{x}) \tag{1.11}$$

will also be used.

If a second parallelogram Σ', spanned by $\mathbf{a}'$ and $\mathbf{b}'$ and the offset $\boldsymbol{\xi}_0$, is mapped onto Σ by a (linear) transformation $T : \Sigma' \subset \mathbb{R}^3 \to \Sigma \in \mathbb{R}^3$ with $\boldsymbol{\xi} \mapsto \mathbf{F} \cdot \boldsymbol{\xi}$ and $T(\Sigma') = \Sigma$, then

$$\mathbf{x}_0 = \mathbf{F} \cdot \boldsymbol{\xi}_0 \tag{1.12}$$

$$\mathbf{a} = \mathbf{F} \cdot \mathbf{a}' \tag{1.13}$$

$$\mathbf{b} = \mathbf{F} \cdot \mathbf{b}' \tag{1.14}$$

and the graph of Σ could be written as

$$\mathbf{p}_A(u,v) = \mathbf{F} \cdot \boldsymbol{\xi}_0 + u\mathbf{F} \cdot \mathbf{a}' + v\mathbf{F} \cdot \mathbf{b}' \tag{1.15}$$

$$= \mathbf{F} \cdot \mathbf{p}'_A(u,v). \tag{1.16}$$

Hence, the integral of the first kind could be transformed (or traced back) to Σ' via

$$\int_{\Sigma} f(\mathbf{x})\, dA(\mathbf{x}) = \int_{\Sigma'} f(\mathbf{F} \cdot \boldsymbol{\xi}) |\det(\mathbf{F})| \frac{\left|\left| \mathbf{F}^{-\mathrm{T}} \cdot (\mathbf{a}' \times \mathbf{b}') \right|\right|}{||\mathbf{a}' \times \mathbf{b}'||}\, dA'(\boldsymbol{\xi}). \tag{1.17}$$

Note in this case, since $\mathbf{F}, \mathbf{a}', \mathbf{b}', \mathbf{a}$ and $\mathbf{b}$ are constant, the fraction

$$|\det(\mathbf{F})| \frac{\left|\left| \mathbf{F}^{-\mathrm{T}} \cdot (\mathbf{a}' \times \mathbf{b}') \right|\right|}{||\mathbf{a}' \times \mathbf{b}'||} = \frac{\mathrm{area}\{\Sigma\}}{\mathrm{area}\{\Sigma'\}} \tag{1.18}$$

corresponds to the area change due to the linear transformation T. Another interpretation,

or just typeface, is obtained by identifying

$$\frac{\mathbf{a}' \times \mathbf{b}'}{||\mathbf{a}' \times \mathbf{b}'||} = \mathbf{n}', \tag{1.19}$$

i.e. the unit normal vector of Σ'. The integral transformation due to the linear mapping $T(\boldsymbol{\xi}) = \mathbf{F} \cdot \boldsymbol{\xi}$ with $T(\Sigma') = \Sigma$ of the first kind surface integral could thus be written as

$$\int\limits_{\Sigma} f(\mathbf{x})\, dA(\mathbf{x}) = \int\limits_{\Sigma'} f(\mathbf{F} \cdot \boldsymbol{\xi}) |\det(\mathbf{F})|\, \left|\left|\mathbf{F}^{-\mathrm{T}} \cdot \mathbf{n}'\right|\right|\, dA(\boldsymbol{\xi})'. \tag{1.20}$$

Auxiliary calculation 1.1:

$$\begin{aligned}
\int\limits_{\Sigma} f(\mathbf{x})\, dA(\mathbf{x}) &= \iint\limits_{S} f(\mathbf{p}_A(u,v)) \left|\left|\frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v}\right|\right| d(u,v) \\
&= \iint\limits_{S} f(\mathbf{F} \cdot \mathbf{p}'_A(u,v)) \left|\left|\left(\mathbf{F}\frac{\partial \mathbf{p}'_A}{\partial u}\right) \times \left(\mathbf{F}\frac{\partial \mathbf{p}'_A}{\partial v}\right)\right|\right| d(u,v) \\
&= \iint\limits_{S} f(\mathbf{F} \cdot \mathbf{p}'_A(u,v)) |\det(\mathbf{F})|\, \left|\left|\mathbf{F}^{-\mathrm{T}} \cdot \left(\frac{\partial \mathbf{p}'_A}{\partial u} \times \frac{\partial \mathbf{p}'_A}{\partial v}\right)\right|\right| d(u,v) \\
&= \iint\limits_{S} f(\mathbf{F} \cdot \mathbf{p}'_A(u,v)) |\det(\mathbf{F})|\, \left|\left|\mathbf{F}^{-\mathrm{T}} \cdot (\mathbf{a}' \times \mathbf{b}')\right|\right| d(u,v) \\
&= \iint\limits_{S} f(\mathbf{F} \cdot \mathbf{p}'_A(u,v)) |\det(\mathbf{F})|\, \frac{\left|\left|\mathbf{F}^{-\mathrm{T}} \cdot (\mathbf{a}' \times \mathbf{b}')\right|\right|}{||\mathbf{a}' \times \mathbf{b}'||}\, ||\mathbf{a}' \times \mathbf{b}'||\, d(u,v) \\
&= \int\limits_{\Sigma'} f(\mathbf{F} \cdot \boldsymbol{\xi}) |\det(\mathbf{F})|\, \frac{\left|\left|\mathbf{F}^{-\mathrm{T}} \cdot (\mathbf{a}' \times \mathbf{b}')\right|\right|}{||\mathbf{a}' \times \mathbf{b}'||}\, dA'(\boldsymbol{\xi})
\end{aligned}$$

Generalizing this concept leads to the following lemma.

Lemma 1 (Transformation of surface integrals under linear transformation)**.**

Let Σ' be a surface in $\mathbb{R}^3$ with graph $\mathbf{p}'_A(u,v)$, $(u,v) \in S \subset \mathbb{R}^2$ and $T : \mathbb{R}^3 \to \mathbb{R}^3$ be a linear transformation $T(\boldsymbol{\xi}) = \mathbf{F} \cdot \boldsymbol{\xi}$, $\boldsymbol{\xi} \in \Sigma'$. Further, let Σ be the (embedded) surface in $\mathbb{R}^3$ with $\Sigma = T(\Sigma')$ and $\det(\mathbf{F}) \neq 0\ \forall \boldsymbol{\xi} \in \Sigma'$. Then, for $\mathbf{x} \in \Sigma$ and $\mathbf{x} = T(\boldsymbol{\xi}) = \mathbf{F} \cdot \boldsymbol{\xi}$

$$\int\limits_{\Sigma} f(\mathbf{x})\, dA(\mathbf{x}) = \int\limits_{\Sigma'} f(\mathbf{F} \cdot \boldsymbol{\xi}) |\det(\mathbf{F})|\, \left|\left|\mathbf{F}^{-\mathrm{T}} \cdot \mathbf{n}'\right|\right|\, dA'(\boldsymbol{\xi}) \tag{1.21}$$

$$= \int\limits_{\Sigma'} f(\mathbf{F} \cdot \boldsymbol{\xi})\, |\det(\mathbf{F})|\, \left|\left|\mathbf{F}^{-\mathrm{T}} \cdot \left(\frac{\partial \mathbf{p}'_A}{\partial u} \times \frac{\partial \mathbf{p}'_A}{\partial v}\right)\Big|_{\boldsymbol{\xi}}\right|\right|\, dA'(\boldsymbol{\xi}). \tag{1.22}$$

Clearly, this lemma could be further generalized to arbitrary diffeomorphisms mapping Σ' onto Σ.

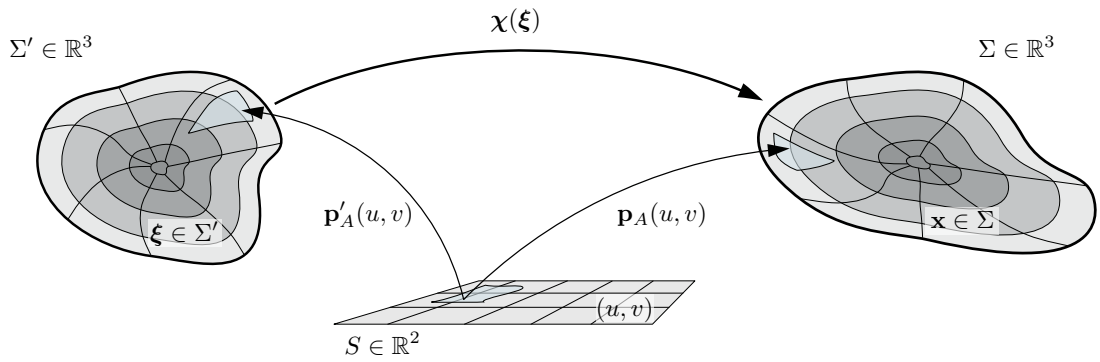

Figure 1.3.: The diffeomorphism $\boldsymbol{\chi} : \mathbb{R}^3 \to \mathbb{R}^3$ maps the embedded surface Σ' onto Σ. The parametrization of Σ' is $\mathbf{p}'_A(u,v)$ while the parametrization of Σ is $\mathbf{p}_A(u,v)$. Even though Σ' and Σ belong to the same parametric domain S, for a given pair (u^*, v^*) in general $\mathbf{p}'_A(u^*, v^*) \neq \mathbf{p}_A(u^*, v^*)$.

Theorem 1 (Transformation of surface integrals under diffeomorphisms)**.**

Let Σ' be a regular surface in $\mathbb{R}^3$ with graph $\mathbf{p}'_A(u,v),\ (u,v) \in S \subset \mathbb{R}^2$ and let $\boldsymbol{\chi} : \Sigma' \to \Sigma \subset \mathbb{R}^3$ be a diffeomorphism with $\Sigma' \ni \boldsymbol{\xi} \mapsto \boldsymbol{\chi}(\boldsymbol{\xi}) = \mathbf{x} \in \Sigma$. Then the graph of Σ is given by $\mathbf{p}_A(u,v) = \boldsymbol{\chi}(\mathbf{p}'_A(u,v)),\ (u,v) \in S$ and Σ is regular. If the vector gradient or Jacobian of $\boldsymbol{\chi}$ is abbreviated as

$$\boldsymbol{\nabla}\boldsymbol{\chi}(\boldsymbol{\xi}) =: \mathbf{F}(\boldsymbol{\xi}) \tag{1.23}$$

then the **surface integral of the first kind** transforms as

$$\int_{\Sigma} f(\mathbf{x})\, dA(\mathbf{x}) = \int_{\Sigma'} |\det(\mathbf{F})|\, f(\boldsymbol{\chi}(\boldsymbol{\xi}))\, \left\| \mathbf{F}^{-\mathrm{T}}(\boldsymbol{\xi}) \cdot \mathbf{n}(\boldsymbol{\xi})' \right\|\, dA'(\boldsymbol{\xi}) \tag{1.24}$$

and the **surface integral of the second kind** as

$$\int_{\Sigma} \mathbf{f}^{\mathrm{T}}(\mathbf{x}) \cdot\, d\mathbf{A}(\mathbf{x}) = \int_{\Sigma'} \det(\mathbf{F})\ \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi})) \cdot \mathbf{F}^{-\mathrm{T}}(\boldsymbol{\xi}) \cdot\, d\mathbf{A}'(\boldsymbol{\xi}) \tag{1.25}$$

$$= \int_{\Sigma'} \det(\mathbf{F})\ \left\langle \mathbf{F}^{-1}(\boldsymbol{\xi}) \cdot \mathbf{f}(\boldsymbol{\chi}(\boldsymbol{\xi})),\, d\mathbf{A}'(\boldsymbol{\xi}) \right\rangle. \tag{1.26}$$

Proof. Since $\boldsymbol{\chi}$ is a diffeomorphism $\det(\mathbf{F}) \neq 0$. From the definition of the surface integral, one writes

$$\int_{\Sigma} f(\mathbf{x})\, dA(\mathbf{x}) = \iint_{S} f(\mathbf{p}_A(u,v)) \left\| \frac{\partial\, \mathbf{p}_A}{\partial\, u} \times \frac{\partial\, \mathbf{p}_A}{\partial\, v} \right\|\, d(u,v). \tag{1.27}$$

With $\mathbf{p}_A(u,v) = \boldsymbol{\chi}(\mathbf{p}'_A(u,v))$ one obtains thus

$$\left\| \frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v} \right\| \tag{1.28}$$

$$= \left\| \left(\boldsymbol{\nabla}\boldsymbol{\chi} \frac{\partial \mathbf{p}'_A}{\partial u} \right) \times \left(\boldsymbol{\nabla}\boldsymbol{\chi} \frac{\partial \mathbf{p}'_A}{\partial v} \right) \right\| \tag{1.29}$$

$$\overset{\text{eq. (A.6)}}{=} |\det(\mathbf{F}(\mathbf{p}'_A(u,v)))| \cdot \left\| \mathbf{F}^{-\mathrm{T}}(\mathbf{p}'_A(u,v)) \cdot \left(\frac{\partial \mathbf{p}'_A}{\partial u} \times \frac{\partial \mathbf{p}'_A}{\partial v} \right) \right\| \tag{1.30}$$

$$= |\det(\mathbf{F}(\mathbf{p}'_A(u,v)))| \cdot \left\| \mathbf{F}^{-\mathrm{T}}(\mathbf{p}'_A(u,v)) \cdot \underbrace{\frac{\frac{\partial \mathbf{p}'_A}{\partial u} \times \frac{\partial \mathbf{p}'_A}{\partial v}}{\left\| \frac{\partial \mathbf{p}'_A}{\partial u} \times \frac{\partial \mathbf{p}'_A}{\partial v} \right\|}}_{\mathbf{n}(\boldsymbol{\xi})} \right\| \cdot \left\| \frac{\partial \mathbf{p}'_A}{\partial u} \times \frac{\partial \mathbf{p}'_A}{\partial v} \right\| \tag{1.31}$$

$$= |\det(\mathbf{F}(\boldsymbol{\xi}))| \cdot \left\| \mathbf{F}^{-\mathrm{T}}(\boldsymbol{\xi}) \cdot \mathbf{n}'(\boldsymbol{\xi}) \right\| \cdot \left\| \frac{\partial \mathbf{p}'_A}{\partial u} \times \frac{\partial \mathbf{p}'_A}{\partial v} \right\| \Big|_{\boldsymbol{\xi}} \tag{1.32}$$

where $\left\| \frac{\partial \mathbf{p}'_A}{\partial u} \times \frac{\partial \mathbf{p}'_A}{\partial v} \right\| \neq 0$ since Σ is regular (*i.e.* $\frac{\partial \mathbf{p}'_A}{\partial u}$ and $\frac{\partial \mathbf{p}'_A}{\partial v}$ are linear independent $\forall (u,v) \in S$). Hence

$$\int_\Sigma f(\mathbf{x})\, dA(\mathbf{x}) = \iint_S f(\boldsymbol{\chi}(\mathbf{p}'_A(u,v))) \cdot |\det(\mathbf{F}(\mathbf{p}'_A(u,v)))| \cdot \left\| \mathbf{F}^{-\mathrm{T}}(\mathbf{p}'_A(u,v)) \cdot \mathbf{n}'(\mathbf{p}'_A(u,v)) \right\| \cdot \left\| \frac{\partial \mathbf{p}'_A}{\partial u} \times \frac{\partial \mathbf{p}'_A}{\partial v} \right\| d(u,v) \tag{1.33}$$

$$= \int_{\Sigma'} f(\boldsymbol{\chi}(\boldsymbol{\xi})) \cdot |\det(\mathbf{F}(\boldsymbol{\xi}))| \cdot \left\| \mathbf{F}^{-\mathrm{T}}(\boldsymbol{\xi}) \cdot \mathbf{n}'(\boldsymbol{\xi}) \right\| dA(\boldsymbol{\xi}). \tag{1.34}$$

Quite similar, the definition of the second kind surface integral

$$\int_\Sigma \mathbf{f}^{\mathrm{T}}(\mathbf{x}) \cdot d\mathbf{A}(\mathbf{x}) = \iint_S \mathbf{f}^{\mathrm{T}}(\mathbf{p}_A(u,v)) \cdot \left(\frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v} \right) d(u,v). \tag{1.35}$$

together with

$$\frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v} = \det(\mathbf{F}(\mathbf{p}'_A(u,v)))\ \mathbf{F}^{-\mathrm{T}}(\mathbf{p}'_A(u,v)) \cdot \left(\frac{\partial \mathbf{p}'_A}{\partial u} \times \frac{\partial \mathbf{p}'_A}{\partial v} \right) \tag{1.36}$$

leads to

$$\int_\Sigma \mathbf{f}^{\mathrm{T}}(\mathbf{x}) \cdot d\mathbf{A}(\mathbf{x}) = \iint_S \det(\mathbf{F}(\mathbf{p}'_A(u,v)))\ \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\mathbf{p}'_A(u,v))) \cdot \mathbf{F}^{-\mathrm{T}}(\mathbf{p}'_A(u,v)) \cdot \left(\frac{\partial \mathbf{p}'_A}{\partial u} \times \frac{\partial \mathbf{p}'_A}{\partial v} \right) d(u,v) \tag{1.37}$$

$$= \int_{\Sigma'} \det(\mathbf{F}(\boldsymbol{\xi}))\ \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi})) \cdot \mathbf{F}^{-\mathrm{T}}(\boldsymbol{\xi}) \cdot d\mathbf{A}(\boldsymbol{\xi}). \tag{1.38}$$

□

Remark 1 (Nanson's formula or relation).

The relationship

$$d\mathbf{A} = |\det(\mathbf{F})|\mathbf{F}^{-\mathrm{T}}(\boldsymbol{\xi})\, d\mathbf{A}' \tag{1.39}$$

between the *differential* $d\mathbf{A}$ and $d\mathbf{A}'$, which one might conclude from equation (1.25), is often called **Nanson's formula** or relation.

Volume integral transformations

Similar to the derivation of surface integral transformations, I will start with a brief derivation of volume integrals based on parallelepipeds and linear transformations of those. This will then be generalized to diffeomorphisms on regular volumes and thus lead to the volume integral transformation (*i.e.* multivariate integral substitution).

Let Ω be a parallelepiped spanned by $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ and the offset $\mathbf{x}_0$, *i.e.* the graph of Ω is given by

$$\mathbf{p}_V(u,v,w) = \mathbf{x}_0 + u\,\mathbf{a} + v\,\mathbf{b} + w\,\mathbf{c} \quad (u,v,w) \in V = [0,1]^3 \tag{1.40}$$

with $\Omega = \mathbf{p}_V(V) \subset \mathbb{R}^3$. The volume of Ω is calculated via

$$\begin{aligned}
\mathrm{vol}\{\Omega\} = \int_\Omega dV &= \iiint_V \left|\left(\left\langle \frac{\partial\,\mathbf{p}_V}{\partial\,u}, \frac{\partial\,\mathbf{p}_V}{\partial\,v} \times \frac{\partial\,\mathbf{p}_V}{\partial\,w}\right\rangle\right)\right| d(u,v,w) && (1.41)\\
&= \iiint_V |\det((\mathbf{a},\mathbf{b},\mathbf{c}))|\, d(u,v,w) && (1.42)\\
&= |\det((\mathbf{a},\mathbf{b},\mathbf{c}))| && (1.43)
\end{aligned}$$

This motivates the following definition of the volume integral.

Definition 2 (Volume integral)**.**

Let a geometric object Ω in the three dimensional space be parametrized by some graph $\mathbf{p}_V(u,v,w)$, $(u,v,w) \in V = [0,1]^3$ with a regular volume $\Omega = \mathbf{p}_V(V)$ (*i.e.* $\frac{\partial\,\mathbf{p}_V}{\partial\,u}, \frac{\partial\,\mathbf{p}_V}{\partial\,v}$, and $\frac{\partial\,\mathbf{p}_V}{\partial\,w}$ are pairwise linear independent). The volume integral of a function $f(\mathbf{x})$, $\mathbf{x} \in \Omega$ over Ω is then defined as

$$\int_\Omega f(\mathbf{x})\, dV(\mathbf{x}) := \iiint_V f(\mathbf{p}_V(u,v,w)) \left|\left\langle \frac{\partial\,\mathbf{p}_V}{\partial\,u}, \left(\frac{\partial\,\mathbf{p}_V}{\partial\,v} \times \frac{\partial\,\mathbf{p}_V}{\partial\,w}\right)\right\rangle\right| d(u,v,w). \tag{1.44}$$

Consider another parallelepiped Ω' (spanned by $\boldsymbol{\xi}_0$, $\mathbf{a}'$,$\mathbf{b}'$ and $\mathbf{c}'$) with graph $\mathbf{p}'_V(u,v,w)$, $(u,v,w) \in [0,1]^3$, $\Omega' = \mathbf{p}'_V(V)$, and a linear transformation T, mapping Ω' onto Ω, *i.e.* $T(\Omega') = \Omega$. Then the graph of Ω is obviously

$$\begin{aligned}
\mathbf{p}_V(u,v,w) &= \mathbf{F}\cdot\mathbf{p}'_V(u,v,w) \qquad (u,v,w) \in [0,1]^3 = V && (1.45)\\
&= \mathbf{F}\cdot\boldsymbol{\xi}_0 + u\mathbf{F}\cdot\mathbf{a}' + v\mathbf{F}\cdot\mathbf{b}' + w\mathbf{F}\cdot\mathbf{c}' && (1.46)
\end{aligned}$$

and the volume integral of some arbitrary function $f(\mathbf{x})$, $\mathbf{x} \in \Omega$ over Ω could be traced back to Ω' via

$$\int_\Omega f(\mathbf{x})\, dV(\mathbf{x}) = \int_{\Omega'} f(\mathbf{F}\cdot\boldsymbol{\xi})|\det(\mathbf{F})|\, dV'(\boldsymbol{\xi}). \tag{1.47}$$

Auxiliary calculation 1.2:

$$
\begin{aligned}
\int\limits_{\Omega} f(\mathbf{x})\, dV(\mathbf{x}) &= \iiint\limits_{V} f(\mathbf{p}_V(u,v,w)) \left| \left\langle \frac{\partial \mathbf{p}_V}{\partial u}, \left(\frac{\partial \mathbf{p}_V}{\partial v} \times \frac{\partial \mathbf{p}_V}{\partial w} \right) \right\rangle \right| d(u,v,w) \\
&= \iiint\limits_{V} f(\mathbf{F}\cdot\mathbf{p}'_V(u,v,w)) \left| (\mathbf{F}\cdot\mathbf{a}')^{\mathrm{T}} \cdot \Big((\mathbf{F}\cdot\mathbf{b}') \times (\mathbf{F}\cdot\mathbf{c}') \Big) \right| d(u,v,w) \\
&= \iiint\limits_{V} f(\mathbf{F}\cdot\mathbf{p}'_V) |\det(\mathbf{F})| \cdot \left| (\mathbf{F}\cdot\mathbf{a}')^{\mathrm{T}} \cdot \mathbf{F}^{-\mathrm{T}} \cdot (\mathbf{b}'\times\mathbf{c}') \right| d(u,v,w) \\
&= \iiint\limits_{V} f(\mathbf{F}\cdot\mathbf{p}'_V) |\det(\mathbf{F})| \cdot |\langle \mathbf{a}', \mathbf{b}'\times\mathbf{c}' \rangle| \, d(u,v,w) \\
&= \iiint\limits_{V} f(\mathbf{F}\cdot\mathbf{p}'_V) |\det(\mathbf{F})| \cdot \left| \left\langle \frac{\partial \mathbf{p}'_V}{\partial u}, \left(\frac{\partial \mathbf{p}'_V}{\partial v} \times \frac{\partial \mathbf{p}'_V}{\partial w} \right) \right\rangle \right| d(u,v,w) \\
&= \int\limits_{\Omega'} f(\mathbf{F}\cdot\boldsymbol{\xi}) |\det(\mathbf{F})| \, dV'(\boldsymbol{\xi}).
\end{aligned}
$$

Clearly, one is not restricted to parallelepipeds as volume objects in $\mathbb{R}^3$, which states the following lemma.

Lemma 2 (Transformation of volume integrals under linear transformations)**.**

Let Ω' be a volume element in $\mathbb{R}^3$ with graph $\mathbf{p}'_V(u,v,w)$, $(u,v,w) \in V \subset \mathbb{R}^3$ and $T : \mathbb{R}^3 \to \mathbb{R}^3$ be a linear transformation $T(\boldsymbol{\xi}) = \mathbf{F}\cdot\boldsymbol{\xi}$, $\boldsymbol{\xi} \in \Omega'$. Further, let Ω be the volume obtained from from the linear transformation of Ω', *i.e.* $\Omega = T(\Omega')$, and $\det(\mathbf{F}) \neq 0$. Then, for $\mathbf{x} = T(\boldsymbol{\xi}) = \mathbf{F}\cdot\boldsymbol{\xi}$ the volume integral transforms according to

$$
\int\limits_{\Omega} f(\mathbf{x})\, dV(\mathbf{x}) = \int\limits_{\Omega'} f(\mathbf{F}\cdot\boldsymbol{\xi}) |\det(\mathbf{F})| \, dV'(\boldsymbol{\xi}). \tag{1.48}
$$

Again, one is not restricted to linear transformations but could derive an integral transformation for general diffeomorphisms.

Theorem 2 (Transformation of volume integrals under diffeomorphisms)**.**

Let Ω' be a regular volume in $\mathbb{R}^3$ with graph $\mathbf{p}'_V(u,v,w)$, $(u,v,w) \in V \subset \mathbb{R}^3$ and let $\boldsymbol{\chi} : \Omega' \to \Omega \subset \mathbb{R}^3$ be a diffeomorphism with $\Omega' \ni \boldsymbol{\xi} \mapsto \boldsymbol{\chi}(\boldsymbol{\xi}) = \mathbf{x} \in \Omega$. Then the graph of Ω is given by $\mathbf{p}_V(u,v,w) = \boldsymbol{\chi}(\mathbf{p}'_V(u,v,w))$, $(u,v,w) \in V$ and Ω is regular. If the vector gradient or jacobian of $\boldsymbol{\chi}$ is abbreviated as

$$
\boldsymbol{\nabla}\boldsymbol{\chi}(\boldsymbol{\xi}) =: \mathbf{F}(\boldsymbol{\xi}) \tag{1.49}
$$

then the volume integral transforms as

$$
\int\limits_{\Omega} f(\mathbf{x})\, dA(\mathbf{x}) = \int\limits_{\Omega'} f(\boldsymbol{\chi}(\boldsymbol{\xi})) |\det(\mathbf{F}(\boldsymbol{\xi}))| \, dA'(\boldsymbol{\xi}). \tag{1.50}
$$

Proof. The proof is straight forward derived from equations (1.47)-(1.48) since the vector gradient $\boldsymbol{\nabla}\boldsymbol{\chi}$ is a linear map. □

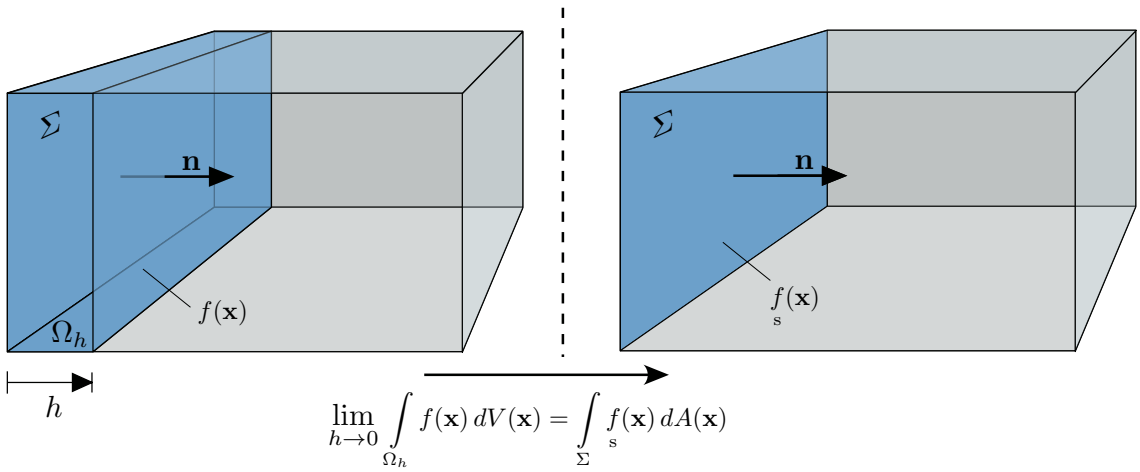

Figure 1.4.: Formal derivation of a surface field $\underset{\mathrm{s}}{f}(\mathbf{x})$ from a vanishing volume element and a volume density $f(\mathbf{x})$.

Besides the definition (1.8) of the surface integral of the first kind, one could also deduce the surface integral from a limit process of some volume integral. Consider a surface $\Sigma \in \mathbb{R}^3$ embedded in a parallel volume element Ω_h as shown in figure 1.4 . The surface Σ obeys the parametrization $\mathbf{p}_A(u,v)$, $(u,v) \in S$ with $\Sigma = \mathbf{p}_A(S)$ and

$$\mathbf{n} = \frac{\frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v}}{\left\| \frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v} \right\|} \tag{1.51}$$

Hence, Ω_h is *parametrized* by

$$\mathbf{p}_V(u,v,w) = \mathbf{p}_A(u,v) + h \cdot w\,\mathbf{n} \quad (u,v,w) \in [0,1]^3 = V \tag{1.52}$$

and

$$\left\langle \frac{\partial \mathbf{p}_V}{\partial w}, \frac{\partial \mathbf{p}_V}{\partial u} \times \frac{\partial \mathbf{p}_V}{\partial v} \right\rangle = h \left\langle \mathbf{n}, \frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v} \right\rangle \tag{1.53}$$

$$= h \left\| \frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v} \right\| \tag{1.54}$$

Next, consider a scalar field $\mathbf{f}$ which is a **volumetric density** of some finite integral value F_h, *i.e.*

$$F_h = \int_{\Omega_h} f(\mathbf{x})\, dV(\mathbf{x}). \tag{1.55}$$

At some fixed position $\mathbf{x}$ one could build a small envelope of height h in normal direction around some surface Σ and write the volume density as

$$f(\mathbf{x}) \approx \frac{1}{h} \underset{\mathrm{s}}{f}(\mathbf{x}), \tag{1.56}$$

where $\underset{\mathrm{s}}{f}$ is the corresponding **surface density**. Note that $\underset{\mathrm{s}}{f}$ is a surface density (2D measure) while f is a volume density (*i.e.* 3D measure). Building hence the limit $h \to 0$

one derives the surface value of $\underset{\mathrm{s}}{F} = \lim_{h\to 0} F_h$ as

$$\underset{\mathrm{s}}{F} = \lim_{h\to 0} \int\limits_{\Omega_h} f(\mathbf{x})\, dV(\mathbf{x}) \tag{1.57}$$

$$= \lim_{h\to 0} \iiint\limits_{V} \frac{1}{h} \underset{\mathrm{s}}{f}(\mathbf{p}_V(u,v,w)) \left\langle \frac{\partial \mathbf{p}_V}{\partial w}, \frac{\partial \mathbf{p}_V}{\partial u} \times \frac{\partial \mathbf{p}_V}{\partial v} \right\rangle d(u,v,w) \tag{1.58}$$

$$= \iiint\limits_{V} \lim_{h\to 0} \underset{\mathrm{s}}{f}(\mathbf{p}_V(u,v,w)) \left\| \frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v} \right\| d(u,v,w) \tag{1.59}$$

$$= \iint\limits_{S} \underset{\mathrm{s}}{f}(\mathbf{p}_A(u,v)) \left\| \frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v} \right\| d(u,v) \tag{1.60}$$

$$= \int\limits_{\Sigma} \underset{\mathrm{s}}{f}(\mathbf{x})\, dA(\mathbf{x}). \tag{1.61}$$

However, the rigorous definition of surface fields is a longstanding discussion, which started with the work of J.W. Gibbs on surface tension. In this work I will always assume either an interface has no independent existence, and thus no explicit surface field, or I will state an explicit surface field. For further discussions on the derivation of surface fields I refer to [4].

Line integrals

Beside surface and volume integrals, line integrals over some parametric curves in the three dimensional space (*e.g.* a conductor loop) arise in the theory of balance equations and transport theorems. However, the overall derivation is abbreviated and only the definitions of the different kinds of line integrals as well as their transformation laws under diffeomorphisms are given.

Definition 3 (Line integral of the first and second kind)**.**

Let a curve C in the three dimensional space be parametrized by some graph $\mathbf{p}_C(u)$, $u \in L = [0,1]$ with a piecewise smooth curve $\Psi_C = \mathbf{p}_C(L)$. The **line integral of the first kind** for a function $f(\mathbf{x})$, $\mathbf{x} \in \Psi_C$ over the curve C is then defined as

$$\int\limits_{\Psi_C} f(\mathbf{x})\, ds(\mathbf{x}) := \int\limits_{L} f(\mathbf{p}_C(u)) \left\| \frac{\partial \mathbf{p}_C}{\partial u} \right\| du \tag{1.62}$$

and the **line integral of the second kind** for a vector field $\mathbf{f}(\mathbf{x}) \in \mathbb{R}^3$ as

$$\int\limits_{\Psi_C} \mathbf{f}(\mathbf{x})^{\mathrm{T}} \cdot d\mathbf{s}(\mathbf{x}) := \int\limits_{L} \left\langle \mathbf{f}(\mathbf{p}_C(u)), \frac{\partial \mathbf{p}_C}{\partial u} \right\rangle du. \tag{1.63}$$

The length of a curve C is then simply obtained as

$$\mathrm{len}\{\mathrm{C}\} = \int_{\Psi_C} 1\, ds(\mathbf{x}) = \int_{L} \left\| \frac{\partial \mathbf{p}_C}{\partial u} \right\| du. \tag{1.64}$$

Theorem 3 (Transformation of line integrals under diffeomorphisms)**.**

Let Ψ' be a smooth curve in $\mathbb{R}^3$ with graph $\mathbf{p}'_C(u)$, $u \in L \subset \mathbb{R}$ and let $\boldsymbol{\chi} : \Psi' \to \Psi \subset \mathbb{R}^3$ be diffeomorphism with $\Psi' \ni \boldsymbol{\xi} \mapsto \boldsymbol{\chi}(\boldsymbol{\xi}) = \mathbf{x} \in \Psi$, Then the graph of Ψ is given by

$\mathbf{p}_C(u) = \boldsymbol{\chi}(\mathbf{p}'_C(u))$, $u \in L$ and Ψ is smooth. Abbreviating again $\boldsymbol{\nabla}\boldsymbol{\chi} =: \mathbf{F}$, the line integral of the first kind transforms as

$$\int_{\Psi} f(\mathbf{x})\, ds(\mathbf{x}) = \int_{\Psi'} f(\boldsymbol{\chi}(\boldsymbol{\xi}))\, ||\mathbf{F}(\boldsymbol{\xi}) \cdot \mathbf{n}(\boldsymbol{\xi})||\; ds'(\boldsymbol{\xi}) \tag{1.65}$$

and the line integral of the second kind as

$$\int_{\Psi} \mathbf{f}(\mathbf{x})^{\mathrm{T}} \cdot\, d\mathbf{s}(\mathbf{x}) = \int_{\Psi'} \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi})) \cdot \mathbf{F}(\boldsymbol{\xi})\, d\mathbf{s}'(\mathbf{x}) \tag{1.66}$$

$$= \int_{\Psi'} \left\langle \mathbf{F}^{\mathrm{T}}(\boldsymbol{\xi}) \cdot \mathbf{f}(\boldsymbol{\chi}(\boldsymbol{\xi})), \mathbf{n}(\boldsymbol{\xi}) \right\rangle\; ds'(\boldsymbol{\xi}) \tag{1.67}$$

Proof. Applying the definitions of the first kind line integral and $\mathbf{p}_C(u) = \boldsymbol{\chi}(\mathbf{p}'_C(u))$ leads to

$$\int_{\Psi} f(\mathbf{x})\, ds(\mathbf{x}) = \int_{L} f(\boldsymbol{\chi}(\mathbf{p}'_C(u))) \cdot \left|\left| \mathbf{F} \cdot \frac{\partial\, \mathbf{p}'_C}{\partial\, u} \right|\right| du \tag{1.68}$$

$$= \int_{L} f(\boldsymbol{\chi}(\mathbf{p}'_C(u))) \cdot \left|\left| \mathbf{F} \cdot \underbrace{\frac{\frac{\partial\, \mathbf{p}'_C}{\partial\, u}}{\left|\left|\frac{\partial\, \mathbf{p}'_C}{\partial\, u}\right|\right|}}_{=\mathbf{n}(\mathbf{p}'_C(u))} \cdot \left|\left| \frac{\partial\, \mathbf{p}'_C}{\partial\, u} \right|\right| \right|\, du \tag{1.69}$$

$$= \int_{\Psi'} f(\boldsymbol{\chi}(\boldsymbol{\xi}))\, ||\mathbf{F}(\boldsymbol{\xi}) \cdot \mathbf{n}(\boldsymbol{\xi})||\; ds'(\boldsymbol{\xi}). \tag{1.70}$$

Similar the transformation of the second kind line integral is derived. □

Tensorial extensions

Due to the vectorial nature of some physical properties, *e.g.* momentum or electric flux, the necessity of volume and surface integrals of vector fields arises. This extension is essentially **column wise** and in general straight forward. However, in the context of dyadic products some useful relationships are derived in this section.

Definition 4 (Vector integral)**.**

Let $\mathbf{f}(s_1, \ldots, s_n) = (f_1(s_1, \ldots, s_n), \ldots, f_m(s_1, \ldots, s_n))^{\mathrm{T}}$ and f_k, $k = 1, \ldots, m$ be integrable. Then

$$\int \mathbf{f}\, d(s_1, \ldots, s_n) := \begin{pmatrix} \int f_1\, d(s_1, \ldots, s_n) \\ \vdots \\ \int f_m\, d(s_1, \ldots, s_n) \end{pmatrix} = \left(\int f_k\, d(s_1, \ldots, s_n) \right)_{k=1,\ldots,m} \in \mathbb{R}^m \tag{1.71}$$

Definition 5 (Volume integral of vector fields)**.**

The volume integral of a vector field $\mathbf{f}(\mathbf{x}) = (f_1(\mathbf{x}), f_2(\mathbf{x}), f_3(\mathbf{x}))$, $\mathbf{x} \in \Omega$ over Ω is defined

as

$$\int_{\Omega} \mathbf{f}(\mathbf{x})\, dV(\mathbf{x}) := \begin{pmatrix} \iiint_V f_1(\mathbf{p}_V(u,v,w)) \left|\left\langle \frac{\partial \mathbf{p}_V}{\partial u}, \left(\frac{\partial \mathbf{p}_V}{\partial v} \times \frac{\partial \mathbf{p}_V}{\partial w}\right)\right\rangle\right| d(u,v,w) \\ \iiint_V f_2(\mathbf{p}_V(u,v,w)) \left|\left\langle \frac{\partial \mathbf{p}_V}{\partial u}, \left(\frac{\partial \mathbf{p}_V}{\partial v} \times \frac{\partial \mathbf{p}_V}{\partial w}\right)\right\rangle\right| d(u,v,w) \\ \iiint_V f_3(\mathbf{p}_V(u,v,w)) \left|\left\langle \frac{\partial \mathbf{p}_V}{\partial u}, \left(\frac{\partial \mathbf{p}_V}{\partial v} \times \frac{\partial \mathbf{p}_V}{\partial w}\right)\right\rangle\right| d(u,v,w). \end{pmatrix} \tag{1.72}$$

Definition 6 (Surface integral of tensor fields)**.**

Let a surface Σ in the three dimensional space be parametrized by some graph $\mathbf{p}_A(u,v)$, $(u,v) \in S = [0,1]^2$ with a regular surface $\Sigma = \mathbf{p}_A(S)$ (*i.e.* $\frac{\partial \mathbf{p}_A}{\partial u}$ and $\frac{\partial \mathbf{p}_A}{\partial v}$ are linear independent). The **surface integral of the first kind** for a vector field $\mathbf{f}(\mathbf{x}) = (f_1(\mathbf{x}), f_3(\mathbf{x}), f_3(\mathbf{x}))^{\mathrm{T}}$, $\mathbf{x} \in \Sigma$ over A is then defined as

$$\int_{\Sigma} \mathbf{f}(\mathbf{x})\, dA(\mathbf{x}) := \begin{pmatrix} \iint_S f_1(\mathbf{p}_A(u,v)) \left\|\frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v}\right\| d(u,v) \\ \iint_S f_2(\mathbf{p}_A(u,v)) \left\|\frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v}\right\| d(u,v) \\ \iint_S f_3(\mathbf{p}_A(u,v)) \left\|\frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v}\right\| d(u,v). \end{pmatrix} \tag{1.73}$$

For a matrix field $\mathbf{F}(\mathbf{x}) = (\mathbf{f}_1, \mathbf{f}_2, \mathbf{f}_3) \in \mathscr{C}^{\infty}(\mathbb{R}^{3\times 3})$, $\mathbf{x} \in \Sigma$ the **surface integral of the second kind** is defined as

$$\int_{\Sigma} \mathbf{F}^{\mathrm{T}}(\mathbf{x}) \cdot\, d\mathbf{A}(\mathbf{x}) := \begin{pmatrix} \iint_S \mathbf{f}_1^{\mathrm{T}}(\mathbf{p}_A(u,v)) \cdot \left(\frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v}\right) d(u,v) \\ \iint_S \mathbf{f}_2^{\mathrm{T}}(\mathbf{p}_A(u,v)) \cdot \left(\frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v}\right) d(u,v) \\ \iint_S \mathbf{f}_3^{\mathrm{T}}(\mathbf{p}_A(u,v)) \cdot \left(\frac{\partial \mathbf{p}_A}{\partial u} \times \frac{\partial \mathbf{p}_A}{\partial v}\right) d(u,v) \end{pmatrix} \tag{1.74}$$

$$= \int_{\Sigma} \mathbf{F}^{\mathrm{T}}(\mathbf{x}) \cdot \mathbf{n}(\mathbf{x})\, dA(\mathbf{x}) \tag{1.75}$$

Corollary 1 (Surface integral of the second kind for a dyadic product)**.**

If a matrix field obeys $\mathbf{F} = \mathbf{g} \otimes \mathbf{h}$ then the surface integral of $\mathbf{F}$ could be written as

$$\int_{\Sigma} (\mathbf{g}(\mathbf{x}) \otimes \mathbf{h}(\mathbf{x}))^{\mathrm{T}} \cdot\, d\mathbf{A}(\mathbf{x}) = \begin{pmatrix} \int_{\Sigma} h_1(\mathbf{x})\, \mathbf{g}^{\mathrm{T}}(\mathbf{x}) \cdot\, d\mathbf{A}(\mathbf{x}) \\ \int_{\Sigma} h_2(\mathbf{x})\, \mathbf{g}^{\mathrm{T}}(\mathbf{x}) \cdot\, d\mathbf{A}(\mathbf{x}) \\ \int_{\Sigma} h_3(\mathbf{x})\, \mathbf{g}^{\mathrm{T}}(\mathbf{x}) \cdot\, d\mathbf{A}(\mathbf{x}) \end{pmatrix} \tag{1.76}$$

$$= \int_{\Sigma} \mathbf{h}(\mathbf{x})\, \mathbf{g}(\mathbf{x})^{\mathrm{T}} \cdot\, d\mathbf{A}(\mathbf{x}) \tag{1.77}$$

$$= \int_{\Sigma} \mathbf{h}(\mathbf{x})\, \langle \mathbf{g}(\mathbf{x}),\, d\mathbf{A}(\mathbf{x}) \rangle \tag{1.78}$$

The last notation is used to emphasize that the result of the integration is indeed a vector again.

Of course, analogous definitions for the line integrals of the first and second kind of vector and matrix fields hold.
The transformation laws of the tensor integrals are also column wise straight forward and will not be discussed explicitly. Only their final transformation, *i.e.* the Reynold transport theorem for vector and matrix fields will be given in section 1.1.3.

1.1.2 Leibniz integral rules

The Leibniz rules for parametric integrals are essentially the prescriptions how to exchange the derivative and the integration of some function, when the integration domain depends on the parameter of which a derivative is desired. This arises when volumes, surfaces or curves are dependent on a time parameter, and the change of an overall property (integral mean) with respect to time is required. Note that the parameter domains of the surface and line integrals remain unchanged, while the embedded surface or curves itself are transformed by the parameter. I will briefly derive the Leibniz rules for volumes, surfaces and line integrals of scalar and vector fields.

Surface integrals

Consider now a parametric surface $\Sigma(t) \in \mathbb{R}^3$ which is allowed to change in time. This is essentially the same as a parameter dependent diffeomorphism $\boldsymbol{\chi}(\boldsymbol{\xi}, t)$ (with $\mathbf{F} = \boldsymbol{\nabla}\boldsymbol{\chi}$) between $\Sigma(t)$ and some (constant) reference surface Σ'. Clearly, theorem 1 is used to compute

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Sigma(t)} \mathbf{f}^{\mathrm{T}}(\mathbf{x}) \cdot d\mathbf{A}(\mathbf{x}) = \frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Sigma'} \det\left(\mathbf{F}(\boldsymbol{\xi}, t)\right) \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi}, t)) \cdot \mathbf{F}^{-\mathrm{T}}(\boldsymbol{\xi}, t) \cdot d\mathbf{A}'(\boldsymbol{\xi}) \tag{1.79}$$

$$\begin{aligned} &= \int\limits_{\Sigma'} \det\left(\mathbf{F}\right) \left(\frac{\mathrm{d}\mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi}, t))}{\mathrm{d}t}\right) \cdot \mathbf{F}^{-\mathrm{T}}\, d\mathbf{A}'(\boldsymbol{\xi}) \\ &\quad + \int\limits_{\Sigma'} \frac{\mathrm{d}(\det\left(\mathbf{F}\right))}{\mathrm{d}t} \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi}, t)) \cdot \mathbf{F}^{-\mathrm{T}}\, d\mathbf{A}'(\boldsymbol{\xi}) \\ &\quad + \int\limits_{\Sigma'} \det\left(\mathbf{F}\right) \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi}, t)) \cdot \frac{\partial \mathbf{F}^{-\mathrm{T}}}{\partial t} \cdot d\mathbf{A}'(\boldsymbol{\xi}) \end{aligned} \tag{1.80}$$

Next, some auxiliary calculations are required.

$$\frac{\partial \boldsymbol{\chi}(\boldsymbol{\xi}, t)}{\partial t} =: \mathbf{v}'(\boldsymbol{\xi}, t) \tag{1.81}$$

$$\frac{\partial \mathbf{F}(\boldsymbol{\xi}, t)}{\partial t} = \frac{\partial \boldsymbol{\nabla}_{\boldsymbol{\xi}}\boldsymbol{\chi}(\boldsymbol{\xi}, t)}{\partial\, \partial t} = \boldsymbol{\nabla}_{\boldsymbol{\xi}}\mathbf{v}'(\boldsymbol{\xi}, t) =: \mathbf{G}(\boldsymbol{\xi}, t) \tag{1.82}$$

If a velocity field $\mathbf{v}(\mathbf{x}, t),\ \mathbf{x} \in \Sigma(t)$ exists, satisfying

$$\mathbf{v}(\mathbf{x}, t) = \mathbf{v}(\boldsymbol{\chi}(\boldsymbol{\xi}, t), t) \equiv \mathbf{v}'(\boldsymbol{\xi}, t) \tag{1.83}$$

one deduces further

$$\boldsymbol{\nabla}_{\boldsymbol{\xi}}\mathbf{v}'(\boldsymbol{\xi}, t) = \boldsymbol{\nabla}_{\boldsymbol{\xi}}\mathbf{v}(\boldsymbol{\chi}(\boldsymbol{\xi}, t), t) = \boldsymbol{\nabla}_{\boldsymbol{\chi}(\boldsymbol{\xi}, t)}\mathbf{v}'(\boldsymbol{\chi}, t) \cdot \boldsymbol{\nabla}_{\boldsymbol{\xi}}\boldsymbol{\chi}(\boldsymbol{\xi}, t) = \boldsymbol{\nabla}_{\mathbf{x}}\mathbf{v}(\mathbf{x}, t) \cdot \mathbf{F}(\boldsymbol{\xi}, t) \tag{1.84}$$

$$\Leftrightarrow \quad \boldsymbol{\nabla}_{\mathbf{x}}\mathbf{v}(\mathbf{x}, t)\big|_{\mathbf{x}=\boldsymbol{\chi}(\boldsymbol{\xi}, t)} = \mathbf{G}(\boldsymbol{\xi}, t) \cdot \mathbf{F}^{-1}(\boldsymbol{\xi}, t) \tag{1.85}$$

and

$$\frac{\mathrm{d}\mathbf{f}(\boldsymbol{\chi}(\boldsymbol{\xi}, t))}{\mathrm{d}t} = \boldsymbol{\nabla}_{\boldsymbol{\chi}(\boldsymbol{\xi}, t)}\mathbf{f}(\boldsymbol{\chi}) \cdot \frac{\partial \boldsymbol{\chi}(\boldsymbol{\xi}, t)}{\partial t} \tag{1.86}$$

$$= \left(\boldsymbol{\nabla}_{\mathbf{x}}\mathbf{f}(\mathbf{x}) \cdot \mathbf{v}(\mathbf{x}, t)\right)\Big|_{\mathbf{x}=\boldsymbol{\chi}(\boldsymbol{\xi}, t)} \tag{1.87}$$

The *right-hand* side of integrals of eq. (1.80) consists of three terms which are now separately rearranged in auxiliary calculations.

Auxiliary calculation 1.3:

$$
\begin{aligned}
&\int\limits_{\Sigma'} \det(\mathbf{F}) \left(\frac{\mathrm{d}\,\mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi},t))}{\mathrm{d}\,t} \right) \cdot \mathbf{F}^{-\mathrm{T}}\, d\mathbf{A}'(\boldsymbol{\xi}) \\
&= \int\limits_{\Sigma'} \det(\mathbf{F}) \left(\mathbf{v}^{\mathrm{T}}(\mathbf{x},t)(\boldsymbol{\nabla}_{\mathbf{x}}\mathbf{f}(\mathbf{x}))^{\mathrm{T}} \right) \Big|_{\mathbf{x}=\boldsymbol{\chi}(\boldsymbol{\xi},t)} \cdot \mathbf{F}^{\mathrm{T}}\, d\mathbf{A}'(\boldsymbol{\xi}) \\
&= \int\limits_{\Sigma(t)} \mathbf{v}^{\mathrm{T}}(\mathbf{x},t) \cdot (\boldsymbol{\nabla}_{\mathbf{x}}\mathbf{f}(\mathbf{x}))^{\mathrm{T}} \cdot\, d\mathbf{A}(\mathbf{x}).
\end{aligned}
$$

Auxiliary calculation 1.4:

$$
\begin{aligned}
&\int\limits_{\Sigma'} \frac{\mathrm{d}\,(\det(\mathbf{F}))}{\mathrm{d}\,t} \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi},t)) \cdot \mathbf{F}^{-\mathrm{T}}\, d\mathbf{A}'(\boldsymbol{\xi}) \\
&= \int\limits_{\Sigma'} \det(\mathbf{F}) \cdot \mathrm{tr}\left(\mathbf{F}^{-1} \frac{\partial\,\mathbf{F}}{\partial\,t} \right) \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi},t)) \cdot \mathbf{F} \cdot\, d\mathbf{A}'(\boldsymbol{\xi}) \\
&= \int\limits_{\Sigma'} \det(\mathbf{F}) \cdot \mathrm{tr}(\boldsymbol{\nabla}_{\mathbf{x}}\mathbf{v}(\mathbf{x},t)) \big|_{\mathbf{x}=\boldsymbol{\chi}(\boldsymbol{\xi},t)} \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi},t)) \cdot \mathbf{F} \cdot\, d\mathbf{A}'(\boldsymbol{\xi}) \\
&= \int\limits_{\Sigma'} \det(\mathbf{F}) \cdot (\mathrm{div}_{\mathbf{x}}\, \mathbf{v}(\mathbf{x},t)) \big|_{\mathbf{x}=\boldsymbol{\chi}(\boldsymbol{\xi},t)} \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi},t)) \cdot \mathbf{F} \cdot\, d\mathbf{A}'(\boldsymbol{\xi}) \\
&= \int\limits_{\Sigma(t)} (\mathrm{div}_{\mathbf{x}}\, \mathbf{v}(\mathbf{x},t))\, \mathbf{f}^{\mathrm{T}}(\mathbf{x}) \cdot\, d\mathbf{A}(\mathbf{x})
\end{aligned}
$$

Auxiliary calculation 1.5:

$$
\begin{aligned}
&\int\limits_{\Sigma'} \det(\mathbf{F})\, \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi},t)) \cdot \frac{\partial \mathbf{F}^{-\mathrm{T}}}{\partial t} \cdot\, d\mathbf{A}'(\boldsymbol{\xi}) \\
&= -\int\limits_{\Sigma'} \det(\mathbf{F})\, \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi},t)) \cdot \left(\mathbf{F}^{-1} \cdot \mathbf{G}(\boldsymbol{\xi},t) \cdot \mathbf{F}^{-1} \right)^{\mathrm{T}} \cdot\, d\mathbf{A}'(\boldsymbol{\xi}) \\
&= -\int\limits_{\Sigma'} \det(\mathbf{F})\, \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi},t)) \cdot \left(\mathbf{F}^{-1} \cdot \boldsymbol{\nabla}_{\mathbf{x}}\mathbf{v}(\mathbf{x},t) \big|_{\mathbf{x}=\boldsymbol{\chi}(\boldsymbol{\xi},t)} \right)^{\mathrm{T}} \cdot\, d\mathbf{A}'(\boldsymbol{\xi}) \\
&= -\int\limits_{\Sigma'} \det(\mathbf{F})\, \mathbf{f}^{\mathrm{T}}(\boldsymbol{\chi}(\boldsymbol{\xi},t)) \cdot \left(\boldsymbol{\nabla}_{\mathbf{x}}\mathbf{v}(\mathbf{x},t) \big|_{\mathbf{x}=\boldsymbol{\chi}(\boldsymbol{\xi},t)} \right)^{\mathrm{T}} \cdot \mathbf{F}^{-\mathrm{T}}\, d\mathbf{A}'(\boldsymbol{\xi}) \\
&= -\int\limits_{\Sigma(t)} \mathbf{f}^{\mathrm{T}}(\mathbf{x}) \cdot (\boldsymbol{\nabla}\mathbf{v}(\mathbf{x},t))^{\mathrm{T}} \cdot\, d\mathbf{A}(\mathbf{x})
\end{aligned}
$$

Inserting the results of the three auxiliary calculations in eq. (1.80) leads to

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Sigma(t)} \mathbf{f}^{\mathrm{T}}(\mathbf{x})\cdot\, d\mathbf{A}(\mathbf{x}) = \int\limits_{\Sigma} \left(\boldsymbol{\nabla}\mathbf{f}\cdot\mathbf{v} + (\operatorname{div}\mathbf{v})\,\mathbf{f} - \boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{f}\right)^{\mathrm{T}}\cdot\, d\mathbf{A}(\mathbf{x}) \tag{1.88}$$

$$\overset{\text{eq. }(A.26)}{=} \int\limits_{\Sigma} \left(\operatorname{Div}(\mathbf{f}\otimes\mathbf{v}) - \boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{f} - (\operatorname{div}\mathbf{f})\,\mathbf{v} + (\operatorname{div}\mathbf{f})\,\mathbf{v}\right)^{\mathrm{T}}\cdot d\mathbf{A}(\mathbf{x}) \tag{1.89}$$

$$\overset{\text{eq. }(A.36)}{=} \int\limits_{\Sigma} \left(\operatorname{curl}(\mathbf{f}\times\mathbf{v}) + (\operatorname{div}\mathbf{f})\,\mathbf{v}\right)^{\mathrm{T}}\cdot d\mathbf{A}(\mathbf{x}) \tag{1.90}$$

$$= \int\limits_{\Sigma} (\operatorname{div}\mathbf{f})\,\mathbf{v}^{\mathrm{T}}\cdot\, d\mathbf{A}(\mathbf{x}) + \oint\limits_{\partial\Sigma} (\mathbf{f}\times\mathbf{v})^{\mathrm{T}}\cdot\, d\mathbf{s}(\mathbf{x}), \tag{1.91}$$

where the last equality was obtained by the Kelvin–Stokes theorem, and thus proofs the following theorem.

Theorem 4 (Leibniz integral rule for second kind surface integrals)**.**

Let $\Sigma(t)$ be a regular surface obtained from a (regular) initial surface Σ' by the diffeomorphism $T : \Sigma' \times I \to \Sigma(t) \times I$ with

$$(\boldsymbol{\xi}, t) \mapsto (\boldsymbol{\chi}(\boldsymbol{\xi}, t), t), \tag{1.92}$$

i.e. $T(I, \Sigma') = (I, \Sigma(t))$. Further, let the motion $\boldsymbol{\chi} \in \mathscr{C}^{\infty}(\mathbb{R}^3)$ and the velocity $\mathbf{v}(\mathbf{x}, t),\ \mathbf{x} \in \Sigma(t)$ satisfy

$$\frac{\partial\,\boldsymbol{\chi}(\boldsymbol{\xi}, t)}{\partial\, t} = \mathbf{v}'(\boldsymbol{\xi}, t) \equiv \mathbf{v}(\boldsymbol{\chi}(\boldsymbol{\xi}, t), t) = \mathbf{v}(\mathbf{x}, t). \tag{1.93}$$

Then the second kind surface integral of (sufficient) smooth vector field $\mathbf{f}(\mathbf{x})$ over a parametric domain satisfies

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Sigma(t)} \mathbf{f}(\mathbf{x})\cdot\, d\mathbf{A}(\mathbf{x}) \tag{1.94}$$

$$= \int\limits_{\Sigma} \left(\operatorname{Div}(\mathbf{f}(\mathbf{x})\otimes\mathbf{v}(\mathbf{x}, t)) - \boldsymbol{\nabla}\mathbf{v}(\mathbf{x}, t)\cdot\mathbf{f}(\mathbf{x})\right)^{\mathrm{T}}\cdot d\mathbf{A}(\mathbf{x}) \tag{1.95}$$

$$= \int\limits_{\Sigma} (\operatorname{div}\mathbf{f}(\mathbf{x}))\,\mathbf{v}(\mathbf{x}, t)^{\mathrm{T}}\cdot\, d\mathbf{A}(\mathbf{x}) + \oint\limits_{\partial\Sigma} (\mathbf{f}(\mathbf{x}, t)\times\mathbf{v}(\mathbf{x}, t))^{\mathrm{T}}\cdot\, d\mathbf{s}(\mathbf{x}) \tag{1.96}$$

Even though the surface integral of the first and second kind look quite similar, they can be inherently different since a surface scalar field $\underset{\mathrm{s}}{f}$ is not necessarily continuously extendable into the surrounding domain. Thus, surface differential operators are required, which are in detail explained in the appendix A.2.

Theorem 5 (Leibniz integral rule for first kind surface integrals)**.**

Let the conditions be similar to theorem 4 and $\underset{\mathrm{s}}{f}$ be a surface field. Then the Leibniz rule

for first kind surface integrals states the following relations,

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Sigma(t)} \underset{\mathrm{s}}{f}(\mathbf{x})\; dA(\mathbf{x}) = \int\limits_{\Sigma(t)} \frac{\mathrm{d}\,\underset{\mathrm{s}}{f}(\mathbf{x})}{\mathrm{d}t} + \underset{\mathrm{s}}{f}\mathrm{div}\,\mathbf{v} - \underset{\mathrm{s}}{f}\,\langle \mathbf{n}, \boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n}\rangle\; dA(\mathbf{x}) \tag{1.97}$$

$$= \int\limits_{\Sigma(t)} \underset{\mathrm{s}}{\mathrm{div}}\left(\underset{\mathrm{s}}{f}\,\mathbf{v}\right)\; dA(\mathbf{x}) \tag{1.98}$$

$$= \int\limits_{\Sigma(t)} (\underset{\mathrm{s}}{\nabla}\underset{\mathrm{s}}{f}(\mathbf{x}))^{\mathrm{T}}\cdot\underset{\mathrm{s}}{\mathbf{v}} + \underset{\mathrm{s}}{f}\;\underset{\mathrm{s}}{\mathrm{div}}\;\underset{\mathrm{s}}{\mathbf{v}} + \underset{\mathrm{s}}{f}v_{\mathbf{n}}\,\kappa\; dA(\mathbf{x}) \tag{1.99}$$

The definitions and derivations of the surface divergence $\underset{\mathrm{s}}{\mathrm{div}}$, surface gradient $\underset{\mathrm{s}}{\nabla}$, the mean curvature κ and the decomposition $\mathbf{v} = \langle \mathbf{v}, \mathbf{n}\rangle\,\mathbf{n} + \underset{\mathrm{s}}{\mathbf{v}} = v_{\mathbf{n}}\,\mathbf{n} + \underset{\mathrm{s}}{\mathbf{v}}$ are given in A.2.

Proof. Let Σ' be the initial surface and $\Sigma(t)$ be obtained from the diffeomorphism $T : (I, \Sigma') \to (I, \Sigma(t)) = (I, \boldsymbol{\chi}(\Sigma', t))$. According to the transformation law for first kind surface integrals (eq. 1.24)

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Sigma(t)} \underset{\mathrm{s}}{f}(\mathbf{x}, t)\, dA = \frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Sigma'} \underset{\mathrm{s}}{f}(\boldsymbol{\chi}(\boldsymbol{\xi}, t))\cdot|\det(\mathbf{F}(\boldsymbol{\xi}, t))|\cdot\left|\left|\mathbf{F}^{-\mathrm{T}}(\boldsymbol{\xi}, t)\cdot\mathbf{n}'(\boldsymbol{\xi})\right|\right|\; dA'(\boldsymbol{\xi}) \tag{1.100}$$

with $\mathbf{F} = \boldsymbol{\nabla}\boldsymbol{\chi}(\boldsymbol{\xi}, t)$. Note that $\mathbf{n}'$ is independent of t, since the initial surface Σ' is assumed to be independent of the parameter (This case will be covered in a following corollary). Some auxiliary calculations are required.

Auxiliary calculation 1.6:

Since $\underset{\mathrm{s}}{f}(\mathbf{x})$ is a surface field, the product rule for surface properties (*c.f.* definition 16 *ff.*) states

$$\frac{\mathrm{d}\,\underset{\mathrm{s}}{f}(\boldsymbol{\chi}(\boldsymbol{\xi}, t))}{\mathrm{d}t} = (\underset{\mathrm{s}}{\nabla}\underset{\mathrm{s}}{f}(\mathbf{x}))^{\mathrm{T}}\cdot\mathbf{v}(\mathbf{x}, t) \quad \mathbf{x}\in\Sigma(t)$$

and $\underset{\mathrm{s}}{\nabla}\underset{\mathrm{s}}{f}(\mathbf{x}) \in T_{\mathbf{x}}(\Sigma(t))$. With the tangential-normal decomposition $\mathbf{v} = \underset{\mathrm{s}}{\mathbf{v}} + v_{\mathbf{n}}\mathbf{n}$ it holds$(\underset{\mathrm{s}}{\nabla} f)^{\mathrm{T}}\cdot\mathbf{v} = (\underset{\mathrm{s}}{\nabla} f)^{\mathrm{T}}\cdot\underset{\mathrm{s}}{\mathbf{v}}$.

Auxiliary calculation 1.7:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left|\left|\underbrace{\mathbf{F}^{-\mathrm{T}}\cdot\mathbf{n}'}_{=:\boldsymbol{\nu}}\right|\right| = \frac{\left\langle \boldsymbol{\nu}, \frac{\mathrm{d}\,\mathbf{F}^{-\mathrm{T}}}{\mathrm{d}t}\cdot\mathbf{n}'\right\rangle}{||\mathbf{F}^{-\mathrm{T}}\cdot\mathbf{n}'||} = -\frac{\langle \boldsymbol{\nu}, (\mathbf{G}\cdot\mathbf{F}^{-1})^{\mathrm{T}}\cdot\mathbf{F}^{\mathrm{T}}\cdot\mathbf{n}'\rangle}{||\boldsymbol{\nu}||}$$

$$= -\left\langle \frac{\boldsymbol{\nu}}{||\boldsymbol{\nu}||}, (\mathbf{G}\cdot\mathbf{F}^{-1})^{\mathrm{T}}\cdot\frac{\boldsymbol{\nu}}{||\boldsymbol{\nu}||}\right\rangle\cdot||\boldsymbol{\nu}||$$

$$= -\left\langle \mathbf{n}, \boldsymbol{\nabla}\mathbf{v}\big|_{\mathbf{x}=\boldsymbol{\chi}(\boldsymbol{\xi},t)}\cdot\mathbf{n}\right\rangle\cdot\left|\left|\mathbf{F}^{-\mathrm{T}}\cdot\mathbf{n}'\right|\right|$$

Hence

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Sigma'} \underset{\mathrm{s}}{f}(\boldsymbol{\chi}(\boldsymbol{\xi},t)) \cdot |\det(\mathbf{F}(\boldsymbol{\xi},t))| \cdot \left\|\mathbf{F}^{-\mathrm{T}}(\boldsymbol{\xi},t)\cdot\mathbf{n}'(\boldsymbol{\xi})\right\| \, dA'(\boldsymbol{\xi}) \tag{1.101}$$

$$= \int\limits_{\Sigma'} \frac{\mathrm{d}\underset{\mathrm{s}}{f}(\boldsymbol{\chi}(\boldsymbol{\xi},t))}{\mathrm{d}t} |\det(\mathbf{F}(\boldsymbol{\xi},t))| \cdot \left\|\mathbf{F}^{-\mathrm{T}}(\boldsymbol{\xi},t)\cdot\mathbf{n}'(\boldsymbol{\xi})\right\| \, dA'(\boldsymbol{\xi}) \tag{1.102}$$

$$+ \int\limits_{\Sigma'} \underset{\mathrm{s}}{f}(\boldsymbol{\chi}(\boldsymbol{\xi},t)) \cdot \operatorname{div}_{\mathbf{x}} \mathbf{v}(\mathbf{x},t)\big|_{\mathbf{x}=\boldsymbol{\chi}(\boldsymbol{\xi},t)} |\det(\mathbf{F}(\boldsymbol{\xi},t))| \cdot \left\|\mathbf{F}^{-\mathrm{T}}(\boldsymbol{\xi},t)\cdot\mathbf{n}'(\boldsymbol{\xi})\right\| \, dA'(\boldsymbol{\xi})$$

$$- \int\limits_{\Sigma'} \underset{\mathrm{s}}{f}(\boldsymbol{\chi}(\boldsymbol{\xi},t)) \cdot \left\langle \mathbf{n}, \boldsymbol{\nabla}\mathbf{v}\big|_{\mathbf{x}=\boldsymbol{\chi}(\boldsymbol{\xi},t)} \cdot \mathbf{n}\right\rangle \cdot |\det(\mathbf{F}(\boldsymbol{\xi},t))| \cdot \left\|\mathbf{F}^{-\mathrm{T}}(\boldsymbol{\xi},t)\cdot\mathbf{n}'(\boldsymbol{\xi})\right\| \, dA'(\boldsymbol{\xi})$$

$$= \int\limits_{\Sigma(t)} (\underset{\mathrm{s}}{\nabla} \underset{\mathrm{s}}{f}(\mathbf{x}))^{\mathrm{T}} \cdot \mathbf{v} + \underset{\mathrm{s}}{f}(\mathbf{x}) \operatorname{div} \mathbf{v}(\mathbf{x},t) - \underset{\mathrm{s}}{f}(\mathbf{x}) \left\langle \mathbf{n}, \boldsymbol{\nabla}\mathbf{v}(\mathbf{x},t)\cdot\mathbf{n}\right\rangle \, dA(\mathbf{x}). \tag{1.103}$$

According to the definitions of the surface divergence

$$\operatorname{div} \mathbf{v} - \langle \mathbf{n}, \boldsymbol{\nabla}\mathbf{v}\cdot\mathbf{n}\rangle = \underset{\mathrm{s}}{\operatorname{div}}\, \mathbf{v}, \tag{1.104}$$

the expression could be further rewritten as

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Sigma(t)} \underset{\mathrm{s}}{f}(\mathbf{x})\, dA = \int\limits_{\Sigma(t)} (\underset{\mathrm{s}}{\nabla} f)^{\mathrm{T}} \cdot \mathbf{v} + \underset{\mathrm{s}}{f} \underset{\mathrm{s}}{\operatorname{div}}\, \mathbf{v}\, dA \tag{1.105}$$

$$= \int\limits_{\Sigma(t)} \underset{\mathrm{s}}{\operatorname{div}}\, (\underset{\mathrm{s}}{f}\mathbf{v})\, dA. \tag{1.106}$$

Splitting the velocity field in its tangential $\underset{\mathrm{s}}{\mathbf{v}}$ and normal component v_n one obtains finally

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Sigma(t)} \underset{\mathrm{s}}{f}(\mathbf{x})\, dA = \int\limits_{\Sigma(t)} \left(\underset{\mathrm{s}}{\operatorname{div}}\, (\underset{\mathrm{s}}{f}\underset{\mathrm{s}}{\mathbf{v}}) + \underset{\mathrm{s}}{f} v_{\mathbf{n}}\, \kappa\right) dA, \tag{1.107}$$

with the curvature $\kappa = \underset{\mathrm{s}}{\operatorname{div}}\, \mathbf{n}$.

Auxiliary calculation 1.8:

Since $\underset{\mathrm{s}}{\nabla}(\underset{\mathrm{s}}{f} v_n) \in T(\Sigma)$ it holds

$$\left\langle \underset{\mathrm{s}}{\nabla}(\underset{\mathrm{s}}{f} v_n), \mathbf{n}\right\rangle = 0$$

and thus

$$\begin{aligned}
\underset{\mathrm{s}}{\operatorname{div}}\, (\underset{\mathrm{s}}{f}\mathbf{v}) &= \underset{\mathrm{s}}{\operatorname{div}}\, (\underset{\mathrm{s}}{f}\underset{\mathrm{s}}{\mathbf{v}}) + \underset{\mathrm{s}}{\operatorname{div}}\, (\underset{\mathrm{s}}{f} v_{\mathbf{n}}\mathbf{n}) \\
&= \underset{\mathrm{s}}{\operatorname{div}}\, (\underset{\mathrm{s}}{f}\underset{\mathrm{s}}{\mathbf{v}}) + \left\langle \underset{\mathrm{s}}{\nabla}(\underset{\mathrm{s}}{f} v_n), \mathbf{n}\right\rangle + \underset{\mathrm{s}}{f} v_n \underset{\mathrm{s}}{\operatorname{div}}\, \mathbf{n} \\
&= \underset{\mathrm{s}}{\operatorname{div}}\, (\underset{\mathrm{s}}{f}\underset{\mathrm{s}}{\mathbf{v}}) + \underset{\mathrm{s}}{f} v_n \kappa
\end{aligned}$$

□

Remark 2 (Material velocity).

A velocity field which satisfies $\mathbf{v}'(\boldsymbol{\xi},t) \equiv \mathbf{v}(\boldsymbol{\chi}(\boldsymbol{\xi},t),t) = \mathbf{v}(\mathbf{x},t)$ is called **material velocity**. This is essentially deduced from a space-time transformation $T : \Sigma' \times I \subset R \to \Sigma(t) \times I$ with $(\boldsymbol{\xi},t) \mapsto T(\boldsymbol{\xi},t) = (\boldsymbol{\chi}(\boldsymbol{\xi},t),t)$ and is investigated in detail in section 1.3.
In general a surface could move with an arbitrary velocity $\mathbf{w}$, which would be determined by the surface momentum balance. In the further work, however, all **singular surfaces** Σ are assumed to **move with the material velocity** and are thus material surfaces, which is sufficient for the sake of this work.

Volume integrals

Clearly, not only time dependent surfaces occur in the derivation of the local balance equations, but mainly time dependent domains $\Omega(t) \subset \mathbb{R}^3$. The Leibniz rule will again be derived by a pullback operation of the transient domain $\Omega(t)$ to some known domain Ω' by a diffeomorphism $(\boldsymbol{\xi},t) \to (\boldsymbol{\chi}(\boldsymbol{\xi},t),t)$. Applying theorem 2 and the auxiliary calculations 1.3 and 1.4 leads to

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Omega(t)} f(\mathbf{x})\,dV(\mathbf{x}) = \frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Omega'} f(\boldsymbol{\chi}(\boldsymbol{\xi},t))\det\left(\mathbf{F}(\boldsymbol{\xi},t)\right)\,dV'(\boldsymbol{\xi}) \tag{1.108}$$

$$= \int\limits_{\Omega'} \langle \nabla_{\mathbf{x}} f(\mathbf{x}), \mathbf{v}(\mathbf{x},t)\rangle\big|_{\mathbf{x}=\boldsymbol{\chi}(\boldsymbol{\xi},t)} \det\left(\mathbf{F}(\boldsymbol{\xi},t)\right)\,dV'(\boldsymbol{\xi})$$

$$+ \int\limits_{\Omega'} (\mathrm{div}_{\mathbf{x}}\,\mathbf{v})\big|_{\mathbf{x}=\boldsymbol{\chi}(\boldsymbol{\xi},t)} \cdot f(\boldsymbol{\chi}(\boldsymbol{\xi},t))\det\left(\mathbf{F}(\boldsymbol{\xi},t)\right)\,dV'(\boldsymbol{\xi}) \tag{1.109}$$

$$= \int\limits_{\Omega(t)} \langle \nabla f(\mathbf{x}), \mathbf{v}(\mathbf{x},t)\rangle + (\mathrm{div}\,\mathbf{v}(\mathbf{x},t))\,f(\mathbf{x})\,dV(\mathbf{x}) \tag{1.110}$$

$$= \int\limits_{\Omega(t)} \mathrm{div}\,(f\cdot\mathbf{v})\,dV(\mathbf{x}) \tag{1.111}$$

Applying the divergence theorem proofs the Leibniz rule for volume integrals.

Theorem 6 (Leibniz rule for volume integrals)**.**

Consider a parametric domain $\Omega(t) \subset \mathbb{R}^3$ with a regular, closed surface $\partial\Omega(t) \in \mathbb{R}^3$ and a diffeomorphism $T : \Omega' \times I \subset \mathbb{R} \to \Omega(t) \times I$ with $(\boldsymbol{\xi},t) \mapsto (\boldsymbol{\chi}(\boldsymbol{\xi},t),t)$ and $T(\Omega',I) = (\Omega(t),I)$. Further, let the motion $\boldsymbol{\chi} \in \mathscr{C}^\infty(\mathbb{R}^3)$ and the velocity $\mathbf{v}(\mathbf{x},t),\ \mathbf{x} \in \Sigma(t)$ satisfy

$$\frac{\partial\,\boldsymbol{\chi}(\boldsymbol{\xi},t)}{\partial\,t} = \mathbf{v}'(\boldsymbol{\xi},t) \equiv \mathbf{v}(\boldsymbol{\chi}(\boldsymbol{\xi},t)) = \mathbf{v}(\mathbf{x},t). \tag{1.112}$$

Then, the exchange order of differentiation with respect to the parameter t and integration with respect to space coordinates $\mathbf{x} \in \Omega$ is computed via

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Omega(t)} f(\mathbf{x})\,dV(\mathbf{x}) = \int\limits_{\Omega(t)} \mathrm{div}\,(f\cdot\mathbf{v})\,dV(\mathbf{x}) \tag{1.113}$$

$$= \oint\limits_{\partial\Omega(t)} (f\cdot\mathbf{v})^{\mathrm{T}}\cdot\,d\mathbf{A}(\mathbf{x}). \tag{1.114}$$

Line integrals

A similar rule for derivatives of parametric line integrals exist, which is stated in the following corollary.

Corollary 2 (Leibniz rule for line integrals of the second kind)**.**

Consider a parametric curve $\Psi(t) \in \mathbb{R}^3$, which is piecewise smooth, and the *boundary* $\partial\Psi(t) \in \mathbb{R}^3$ being the two points $\mathbf{x}^1_\Psi$ and $\mathbf{x}^1_\Psi$. A diffeomorphism $T : \Psi' \times I \subset \mathbb{R} \to \Psi(t) \times I$ maps an initial space curve Ψ' onto $\Psi(t)$, with $(\boldsymbol{\xi}, t) \mapsto (\boldsymbol{\chi}(\boldsymbol{\xi}, t), t)$ and $T(\Omega', I) = (\Omega(t), I)$. Further, let the motion $\boldsymbol{\chi} \in \mathscr{C}^\infty(\mathbb{R}^3)$ and the velocity $\mathbf{v}(\mathbf{x}, t),\ \mathbf{x} \in \Sigma(t)$ satisfy

$$\frac{\partial\, \boldsymbol{\chi}(\boldsymbol{\xi}, t)}{\partial\, t} = \mathbf{v}'(\boldsymbol{\xi}, t) \equiv \mathbf{v}(\boldsymbol{\chi}(\boldsymbol{\xi}, t)) = \mathbf{v}(\mathbf{x}, t). \tag{1.115}$$

Then, the exchange order of differentiation with respect to the parameter t and integration with respect to space coordinates $\mathbf{x} \in \Omega$ is computed via

$$\frac{\mathrm{d}}{\mathrm{d}t} \int\limits_{\Psi(t)} \mathbf{f}^{\mathrm{T}}(\mathbf{x})\, ds(\mathbf{x}) = \int\limits_{\Psi(t)} \Big(\boldsymbol{\nabla}\mathbf{f}(\mathbf{x}) \cdot \mathbf{v}(\mathbf{x}, t) + (\boldsymbol{\nabla}\mathbf{v}(\mathbf{x}, t))^{\mathrm{T}} \cdot \mathbf{f}(\mathbf{x})\Big)^{\mathrm{T}} \cdot\, d\mathbf{s}(\mathbf{x}) \tag{1.116}$$

Proof. The proof is straight forward obtained from the theorem 3. □

Since first kind surface integrals do not arise in the further derivation, it will be not be discussed.

1.1.3 Reynolds transport theorems

Reynolds transport theorems are essentially generalizations of the Leibniz integral rules for explicit time dependent functions, *i.e.* $f(\mathbf{x}) \to f(\mathbf{x}, t),\ \mathbf{f}(\mathbf{x}) \to \mathbf{f}(\mathbf{x}, t)$.

Reynold for surfaces

Theorem 7 (Reynolds transport theorem for surfaces)**.**

Let $\Sigma(t)$ be a regular surface obtained from a (regular) initial surface Σ' by the diffeomorphism $T : \Sigma' \times I \to \Sigma(t) \times I$ with

$$(\boldsymbol{\xi}, t) \mapsto T(\boldsymbol{\xi}, t) = (\boldsymbol{\chi}(\boldsymbol{\xi}, t), t), \tag{1.117}$$

i.e. $T(\Sigma', I) = (\Sigma(t), I)$. Further, let the motion $\boldsymbol{\chi} \in \mathscr{C}^\infty(\mathbb{R}^3)$ and the velocity $\mathbf{v}(\mathbf{x}, t),\ \mathbf{x} \in \Sigma(t)$ satisfy

$$\frac{\partial\, \boldsymbol{\chi}(\boldsymbol{\xi}, t)}{\partial\, t} = \mathbf{v}'(\boldsymbol{\xi}, t) \equiv \mathbf{v}(\boldsymbol{\chi}(\boldsymbol{\xi}, t)) = \mathbf{v}(\mathbf{x}, t). \tag{1.118}$$

Then the second kind surface integral of a (sufficient) smooth vector field $\mathbf{f}(\mathbf{x},t) \in \mathscr{C}^\infty(\mathbb{R}^3)$ over a parametric domain satisfies

$$\frac{\mathrm{d}}{\mathrm{d}t} \int\limits_{\Sigma(t)} \mathbf{f}(\mathbf{x},t) \cdot d\mathbf{A}(\mathbf{x}) \tag{1.119}$$

$$= \int\limits_{\Sigma(t)} \left(\frac{\partial\, \mathbf{f}(\mathbf{x},t)}{\partial\, t} + \mathrm{Div}\,(\mathbf{f}(\mathbf{x},t) \otimes \mathbf{v}(\mathbf{x},t)) - \boldsymbol{\nabla}\mathbf{v}(\mathbf{x},t) \cdot \mathbf{f}(\mathbf{x},t) \right)^{\mathrm{T}} \cdot d\mathbf{A}(\mathbf{x}) \tag{1.120}$$

$$= \int\limits_{\Sigma(t)} \left(\frac{\partial \mathbf{f}(\mathbf{x},t)}{\partial t} + (\mathrm{div}\, \mathbf{f}(\mathbf{x}))\, \mathbf{v}(\mathbf{x},t) \right)^{\mathrm{T}} \cdot d\mathbf{A}(\mathbf{x}) + \oint\limits_{\partial\Sigma(t)} (\mathbf{f}(\mathbf{x}) \times \mathbf{v}(\mathbf{x},t))^{\mathrm{T}} \cdot d\mathbf{s}(\mathbf{x}). \tag{1.121}$$

For a surface field $\underset{\mathrm{s}}{f}(\mathbf{x})$ the first kind integral satisfies

$$\frac{\mathrm{d}}{\mathrm{d}t} \int\limits_{\Sigma(t)} \underset{\mathrm{s}}{f}(\mathbf{x},t)\, dA(\mathbf{x}) = \int\limits_{\Sigma(t)} \frac{\underset{\mathrm{s}}{\mathrm{D}}\, \underset{\mathrm{s}}{f}(\mathbf{x},t)}{\underset{\mathrm{s}}{\mathrm{D}}\, t} + \underset{\mathrm{s}}{f} \mathrm{div}\, \mathbf{v} - \underset{\mathrm{s}}{f} \langle \mathbf{n}, \boldsymbol{\nabla}\mathbf{v} \cdot \mathbf{n} \rangle\, dA(\mathbf{x}) \tag{1.122}$$

$$= \int\limits_{\Sigma(t)} \frac{\partial\, \underset{\mathrm{s}}{f}(\mathbf{x},t)}{\partial\, t} + \underset{\mathrm{s}}{\mathrm{div}}\, (\underset{\mathrm{s}}{f}\mathbf{v})\, dA \tag{1.123}$$

$$= \int\limits_{\Sigma(t)} \frac{\partial\, \underset{\mathrm{s}}{f}(\mathbf{x},t)}{\partial\, t} + \underset{\mathrm{s}}{\mathrm{div}}\, (\underset{\mathrm{s}}{f}\underset{\mathrm{s}}{\mathbf{v}}) + \kappa \cdot \underset{\mathrm{s}}{f} v_{\mathbf{n}}\, dA(\mathbf{x}). \tag{1.124}$$

Proof. The proof is straightforward for the transition $\mathbf{f}(\mathbf{x}) \to \mathbf{f}(\mathbf{x},t)$ an the Leibniz integral rule for surface integrals of the second kind (theorem 4) and of the first kind (theorem 5). The operator

$$\frac{\underset{\mathrm{s}}{\mathrm{D}}}{\underset{\mathrm{s}}{\mathrm{D}}\, t} := \frac{\partial}{\partial\, t} + \mathbf{v}^{\mathrm{T}} \cdot \underset{\mathrm{s}}{\nabla} \tag{1.125}$$

denotes the total (or material) surface derivative. □

Reynold for volumes

The central transport theorem of continuum mechanics is surely Reynolds transport theorem for volume integrals. Since macroscopic extensive physical properties (*e.g.* mass, charge, energy) are defined as volume integral over some respective density, the transport theorem describes the transient evolution of such properties. However, in this section I remain on the mathematical derivation this central theorem of continuum mechanics.

In principle, it follows directly from the Leibniz rule (theorem 6) and the transition $f(\mathbf{x}) \to f(\mathbf{x},t)$. Thus, the scalar field f is said to be implicit and explicit time dependent and the exchange rules of temporal and spatial integration are covered in the following theorem.

Theorem 8 (Reynolds transport theorem for volume integrals)**.**

Let $\Omega(t) \subset \mathbb{R}^3$ be a parametric domain which is obtained from the diffeomorphism $(\boldsymbol{\xi},t) \to (\boldsymbol{\chi}(\boldsymbol{\xi},t),t)$, *i.e.* $\Omega(t) = \boldsymbol{\chi}(\Omega,t)$ with a regular, closed surface $\partial\Omega(t) \in \mathbb{R}^3$, and let f be

a sufficient smooth scalar field $f(\mathbf{x},t)$ $\mathbf{x} \in \Omega(t)$, $t \in I$. If a material velocity $\mathbf{v}(\mathbf{x},t) \in \mathscr{C}^\infty(\mathbb{R}^3)$ exits, obeying

$$\mathbf{v}(\mathbf{x},t) = \mathbf{v}(\boldsymbol{\chi}(\boldsymbol{\xi},t)) \equiv \mathbf{v}'(\boldsymbol{\xi},t) := \frac{\partial\,\boldsymbol{\chi}(\boldsymbol{\xi},t)}{\partial\,t}, \tag{1.126}$$

then the following relation holds, and is called Reynolds transport theorem (for volume integrals),

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Omega(t)} f(\mathbf{x},t)\,dV(\mathbf{x}) = \int\limits_{\Omega(t)} \left(\frac{\mathrm{D}\,f(\mathbf{x},t)}{\mathrm{D}t} + f(\mathbf{x},t)\cdot \operatorname{div}\mathbf{v}(\mathbf{x},t)\right) dV(\mathbf{x}) \tag{1.127}$$

$$= \int\limits_{\Omega(t)} \left(\frac{\partial\,f(\mathbf{x},t)}{\partial\,t} + \operatorname{div}\left(f(\mathbf{x},t)\cdot\mathbf{v}(\mathbf{x},t)\right)\right) dV(\mathbf{x}) \tag{1.128}$$

$$= \int\limits_{\Omega(t)} \frac{\partial\,f(\mathbf{x},t)}{\partial\,t}\,dV(\mathbf{x}) + \oint\limits_{\partial\Omega(t)} \left(f(\mathbf{x},t)\cdot\mathbf{v}(\mathbf{x},t)\right)^{\mathrm{T}} d\mathbf{A}(\mathbf{x}). \tag{1.129}$$

Proof. Again, the proof is straightforward obtained from the Leibniz rule of parametric volume integrals (theorem 6). The operator

$$\frac{\mathrm{D}}{\mathrm{D}t} = \frac{\partial}{\partial\,t} + \mathbf{v}^{\mathrm{T}}\cdot\nabla \tag{1.130}$$

is called total or material derivative. □

Reynold for lines

Finally, a version of Reynolds transport theorem for line integrals of the second kind also exists, and will be given as the following corollary.

Corollary 3 (Reynolds transport theorem for line integrals)**.**

Consider a parametric curve $\Psi(t) \in \mathbb{R}^3$, which is piecewise smooth and a diffeomorphism $T : \Psi' \times I \subset \mathbb{R} \to \Psi(t) \times I$ mapping an initial space curve Ψ' onto $\Psi(t)$, with $(\boldsymbol{\xi},t) \mapsto (\boldsymbol{\chi}(\boldsymbol{\xi},t),t)$ and $T(\Omega',I) = (\Omega(t),I)$. Further, let the velocity $\mathbf{v}(\mathbf{x},t)$ be material, *i.e.*

$$\frac{\partial\,\boldsymbol{\chi}(\boldsymbol{\xi},t)}{\partial\,t} = \mathbf{v}'(\boldsymbol{\xi},t) \equiv \mathbf{v}(\boldsymbol{\chi}(\boldsymbol{\xi},t)) = \mathbf{v}(\mathbf{x},t). \tag{1.131}$$

Then, the exchange order of differentiation with respect to the parameter t and integration with respect to space coordinates $\mathbf{x} \in \Omega$ is computed via

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Psi(t)} \mathbf{f}^{\mathrm{T}}(\mathbf{x})\,ds(\mathbf{x}) \tag{1.132}$$

$$= \int\limits_{\Psi(t)} \left(\frac{\partial\,\mathbf{f}(\mathbf{x},t)}{\partial\,t} + \boldsymbol{\nabla}\mathbf{f}(\mathbf{x},t)\cdot\mathbf{v}(\mathbf{x},t) + \left(\boldsymbol{\nabla}\mathbf{v}(\mathbf{x},t)\right)^{\mathrm{T}}\cdot\mathbf{f}(\mathbf{x},t)\right)^{\mathrm{T}}\cdot\,d\mathbf{s}(\mathbf{x}). \tag{1.133}$$

Tensor valued transport theorems

Central for the later on derived momentum equation is a volume integral of a vector field $\mathbf{f}(\mathbf{x},t)$ over a time dependent domain. The following theorems are straight forward derived from the column wise definitions of volume, surface and vector integrals.

Corollary 4 (Reynolds transport theorem of vector fields for volume integrals)**.**
Let $\Omega(t) \subset \mathbb{R}^3$ be a parametric domain which is obtained from the diffeomorphism $(\boldsymbol{\xi},t) \to (\boldsymbol{\chi}(\boldsymbol{\xi},t),t)$, *i.e.* $\Omega(t) = \boldsymbol{\chi}(\Omega,t)$ with a regular, closed surface $\partial\Omega(t) \in \mathbb{R}^3$, and let $\mathbf{f}$ be a sufficient smooth vector field $\mathbf{f}(\mathbf{x},t)$ $\mathbf{x} \in \Omega(t)$, $t \in I$. If a material velocity $\mathbf{v}(\mathbf{x},t) \in \mathscr{C}^\infty(\mathbb{R}^3)$ exits, obeying

$$\mathbf{v}(\mathbf{x},t) = \mathbf{v}(\boldsymbol{\chi}(\mathbf{x},t),t) \equiv \mathbf{v}'(\boldsymbol{\xi},t) := \frac{\partial\,\boldsymbol{\chi}(\boldsymbol{\xi},t)}{\partial\,t}, \tag{1.134}$$

then the following relation holds, and is called Reynolds transport theorem of vector fields for volume integrals,

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Omega(t)} \mathbf{f}(\mathbf{x},t)\,dV(\mathbf{x}) = \int\limits_{\Omega(t)} \left(\frac{\partial\,\mathbf{f}(\mathbf{x},t)}{\partial\,t} + \mathrm{Div}\,(\mathbf{f}(\mathbf{x},t)\otimes\mathbf{v}(\mathbf{x},t))\right) dV(\mathbf{x}) \tag{1.135}$$

$$= \int\limits_{\Omega(t)} \frac{\partial\,\mathbf{f}(\mathbf{x},t)}{\partial\,t}\,dV(\mathbf{x}) + \oint\limits_{\partial\Omega(t)} (\mathbf{f}(\mathbf{x},t)\otimes\mathbf{v}(\mathbf{x},t))^{\mathrm{T}}\,d\mathbf{A}(\mathbf{x}). \tag{1.136}$$

Since in the later derivation of the momentum equation only time derivatives of vector valued volume integrals occur, Reynolds theorem for surface integrals of vector or tensor functions will not be stated. Note, however, that it is the basis for the momentum balance on surfaces.

1.2 Equations of balance

Each (extensive) scalar physical property $A(t)$ with units $[\mathfrak{U}]$ may be written as

$$A(t) = A^{\Omega}(t) + A^{\Sigma}(t) \tag{1.137}$$

$$= \int\limits_{\Omega} a(\mathbf{x},t)\,dV(\mathbf{x}) + \int\limits_{\Sigma} \underset{\mathrm{s}}{a}(\mathbf{x},t)\,dA(\mathbf{x}), \tag{1.138}$$

where A^{Ω} is called the volume value and A^{Σ} the (singular) surface value of $A(t)$. The respective local fields are the volume density $a(\mathbf{x},t)$ and the surface density $\underset{\mathrm{s}}{a}(\mathbf{x},t)$. The distinction becomes necessary, for example, if a reactive species is present in gas or liquid phase **and** as an adsorbed species on a surface. Note that the surface density $\underset{\mathrm{s}}{a}$ could be derived from the pillbox principle and the limit of an infinitesimal small volume integral (*c.f.* eqn. (1.57) ff). If, however, no singular surface is present $A(t) = A^{\Omega}(t)$.

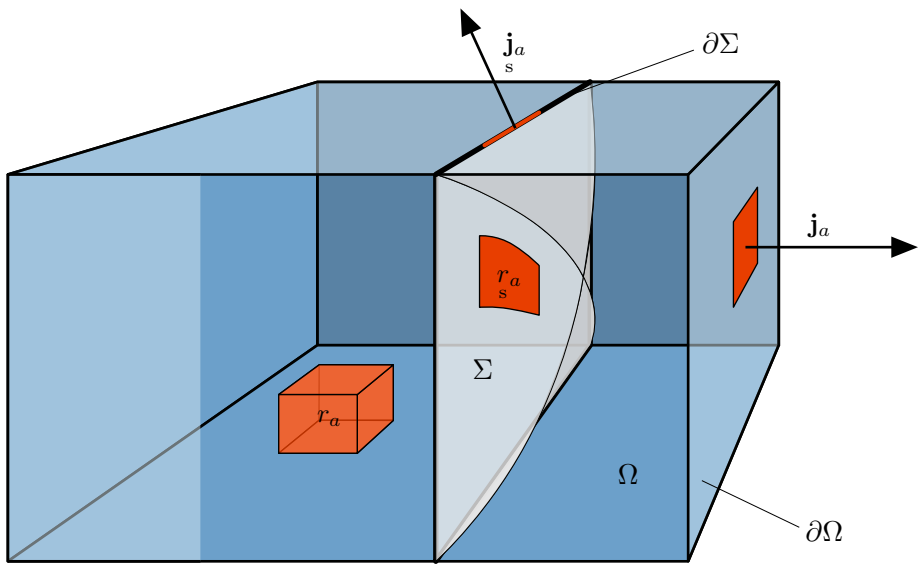

Figure 1.5.: Sketch of the domain Ω containing the (singular) surface Σ with volumetric sources r_a and fluxes as well as surface sources and fluxes.

In this chapter, the mathematical structure of integral equations is investigated, where the macroscopic property $A(t)$ is assumed to change in time due to

- $J_A(t)$, a flux of the property through the boundary of Ω,
- $\underset{\mathrm{s}}{J}_A(t)$, a flux through the boundary of the singular surface Σ,
- $R_A(t)$, volumetric sources or sinks,
- and $\underset{\mathrm{s}}{R}_A(t)$, sources or sinks on the singular surface.

Hence

$$\frac{\mathrm{d}\,A(t)}{\mathrm{d}t} = \frac{\mathrm{d}\,A^{\Omega}(t) + A^{\Sigma}(t)}{\mathrm{d}} = J_A(t) + \underset{\mathrm{s}}{J}_A(t) + R_A(t) + \underset{\mathrm{s}}{R}_A(t), \tag{1.139}$$

and this equation is called **global equation of balance**. Assuming further that flux and source could be described locally, *i.e.*

- the volumetric flux $\mathbf{j}_a(\mathbf{x}, t)$ $\left[\frac{\mathfrak{U}}{\mathrm{m}^2\,\mathrm{s}}\right]$ into Ω with

$$J_A(t) = \oint_{\partial\Omega} \mathbf{j}_a^{\mathrm{T}} \cdot d\mathbf{A},$$

- the (tangential) surface flux $\underset{\mathrm{s}}{\mathbf{j}}_a(\mathbf{x}, t)$ $\left[\frac{\mathfrak{U}}{\mathrm{m}\,\mathrm{s}}\right]$ into Σ with

$$\underset{\mathrm{s}}{J}_A(t)(t) = \oint_{\partial\Sigma} \underset{\mathrm{s}}{\mathbf{j}}_a^{\mathrm{T}} \cdot d\mathbf{s},$$

- the net volumetric production rate $r_a \left[\frac{\mathfrak{U}}{\mathrm{m}^3\,\mathrm{s}}\right]$ with

$$R_A(t) = \int_\Omega r_a \, dV,$$

- and the net surface production $\underset{\mathrm{s}}{r}_a \left[\frac{\mathfrak{U}}{\mathrm{m}^2\,\mathrm{s}}\right]$ with

$$\underset{\mathrm{s}}{R}_A(t) = \int_\Omega \underset{\mathrm{s}}{r}_a \, dA.$$

This assumption is rigorously stated in section 2.1.2 (assumption 2, balance equation representation). The global equation of balance can hence be written as

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\int_\Omega a(\mathbf{x},t)\,dV + \int_\Sigma \underset{\mathrm{s}}{a}(\mathbf{x},t)\,dA(\mathbf{x})\right) = -\int_{\partial\Omega} \mathbf{j}_a(\mathbf{x},t)^{\mathrm{T}} \cdot d\mathbf{A}(\mathbf{x}) - \int_{\partial\Sigma} \underset{\mathrm{s}}{\mathbf{j}}_a(\mathbf{x},t)^{\mathrm{T}} \cdot d\mathbf{s}(\mathbf{x}) + \int_\Omega r_a(\mathbf{x},t)\,dV(\mathbf{x}) + \int_\Sigma \underset{\mathrm{s}}{r}_a(\mathbf{x},t)\,dA(\mathbf{x}). \tag{1.140}$$

The sign of $\mathbf{j}_a(\mathbf{x},t)$ is chosen such that at $\partial\Omega$ the flux points into the domain Ω. Note further that the flux $\mathbf{j}_a(\mathbf{x},t)$ is the net flux of the density a relative to the (possibly) moving domain Ω, and similar $\underset{\mathrm{s}}{\mathbf{j}}_a$ the surface flux with respect to the moving surface Σ.

Of course, a similar global equation of balance holds for a vectorial property $\vec{B}$, and the extension is just straight forward according to the definitions of vectorial integral transformations.

Despite volumetric rate equations, another class of global balance equations arise in the formulation of thermo-electroynamics. Consider a singular surface Σ containing a curve Ψ. Now a (flux) property $C(t)$ is considered with its corresponding flux density $\mathbf{c}(\mathbf{x},t)$, *i.e.*

$$\vec{C}(t) = \int_\Sigma \mathbf{c}^{\mathrm{T}}(\mathbf{x},t) \cdot d\mathbf{A}. \tag{1.141}$$

This global flux property is assumed to change in time due to

- a flow $\vec{J}_C(t)$ through the boundary of Σ with flow density $\mathbf{j}_\mathbf{c}(\mathbf{x},t)$ and

$$\vec{J}_C(t) = -\oint_{\partial\Sigma} \mathbf{j}_\mathbf{c}(\mathbf{x},t)^{\mathrm{T}} \cdot d\mathbf{s},$$

- a production $\vec{R}_C(t)$ on Σ with density $\mathbf{r}_\mathbf{c}(\mathbf{x},t)$ and

$$\vec{R}_C(t) = \int_\Sigma \mathbf{r}_\mathbf{c}(\mathbf{x},t)\,dA$$

- a production $\underset{\mathrm{s}}{\vec{R}}_C(t)$ on Σ with density $\underset{\mathrm{s}}{\mathbf{r}_\mathbf{c}}(\mathbf{x},t)$ with

$$\underset{\mathrm{s}}{\vec{R}}_C(t) = \int_{\partial\Sigma} \underset{\mathrm{s}}{\mathbf{r}_\mathbf{c}}(\mathbf{x},t)\, ds$$

The flux property itself has no corresponding value on the singular line, leading to the **global flux balance equation**

$$\frac{\mathrm{d}C(t)}{\mathrm{d}t} = \vec{J}_C(t) + \vec{R}_C(t) + \underset{\mathrm{s}}{\vec{R}}_C(t) \tag{1.142}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_\Sigma \mathbf{c}^\mathrm{T}(\mathbf{x},t)\cdot\, d\mathbf{A} = -\int_{\partial\Sigma} \mathbf{j}_\mathbf{c}^\mathrm{T}(\mathbf{x},t)\cdot\, d\mathbf{s} + \int_\Sigma \mathbf{r}_\mathbf{c}^\mathrm{T}(\mathbf{x},t)\cdot\, d\mathbf{A} + \int_\Psi \underset{\mathrm{s}}{\mathbf{r}_\mathbf{c}^\mathrm{T}}(\mathbf{x},t)\cdot\, ds. \tag{1.143}$$

1.2.1 Volume balance equations

For domains Ω which contain no singular surface Reynolds transport theorem (8) and the volume divergence theorem 11 are applied to deduce the **global volume equation of balance**, *i.e.*

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_\Omega a(\mathbf{x},t)\, dV = \int_\Omega \frac{\partial\, a(\mathbf{x},t)}{\partial\, t} + \mathrm{div}\ \left(a(\mathbf{x},t)\cdot\mathbf{v}(\mathbf{x},t)\right)\, dV \tag{1.144}$$

$$= -\int_\Omega \mathrm{div}\,\mathbf{j}_a(\mathbf{x},t) - r_a(\mathbf{x},t)\, dV. \tag{1.145}$$

This is yet a global balance equation as the integration is still performed over the whole material domain Ω. Since no operations on the integral itself are performed anymore, one assumes[1] that this relation holds for every $\omega \subset \Omega$, *i.e.*

$$\int_\omega \frac{\partial\, a(\mathbf{x},t)}{\partial\, t} + \mathrm{div}\left(a(\mathbf{x},t)\cdot\mathbf{v}(\mathbf{x},t) + \mathbf{j}_a(\mathbf{x},t)\right) - r_a(\mathbf{x},t)\, dV = 0 \quad \forall\, \omega \subset \Omega, \tag{1.146}$$

which finally leads to the **local volume equation of balance**

$$\frac{\partial\, a(\mathbf{x},t)}{\partial\, t} = -\mathrm{div}\left(a(\mathbf{x},t)\cdot\mathbf{v}(\mathbf{x},t) + \mathbf{j}_a(\mathbf{x},t)\right) + r_a(\mathbf{x},t) \quad \forall \mathbf{x} \in \Omega. \tag{1.147}$$

The term $a(\mathbf{x},t)\cdot\mathbf{v}(\mathbf{x},t) + \mathbf{j}_a(\mathbf{x},t)$ is sometimes abbreviated as total flux $\mathbf{i}_a(\mathbf{x},t)$.

[1] This is raised to the definition of the continuum hypothesis in section 2.1.

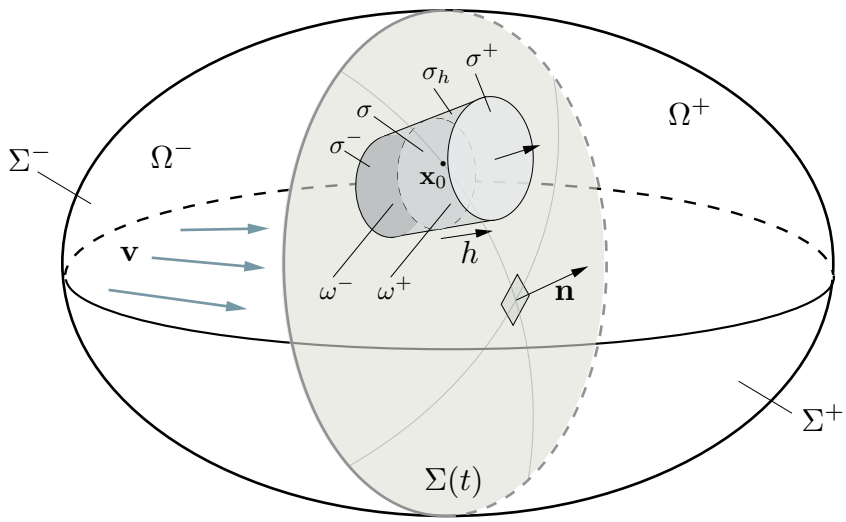

Figure 1.6.: Sketch of a volume element Ω which is divided into Ω^+ and Ω^- by the singular surface Σ. The pillbox $\omega^+ \cup \omega^-$ shrinks to the surface element σ as $h \to 0$.

1.2.2 Surface balance equations

Quite similar to volume properties the local equation of balance for singular surfaces is obtained from a global balance equation and Reynolds theorem for surfaces. The **global equation of balance for singular surfaces** reads

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Sigma} \underset{\mathrm{s}}{a}(\mathbf{x},t)\,dA = \int\limits_{\Sigma} \frac{\partial\, \underset{\mathrm{s}}{a}(\mathbf{x},t)}{\partial\, t} + \underset{\mathrm{s}}{\mathrm{div}}\,(\underset{\mathrm{s}}{a}\,\underset{\mathrm{s}}{\mathbf{v}}) + \kappa\, \underset{\mathrm{s}}{a}(\mathbf{x},t) v_n\; dA \tag{1.148}$$

$$= -\int\limits_{\Sigma} \underset{\mathrm{s}}{\mathrm{div}}\, \underset{\mathrm{s}}{\mathbf{j}_a}(\mathbf{x},t) - \underset{\mathrm{s}}{r_a}(\mathbf{x},t)\, dA \tag{1.149}$$

and is obtained from the Reynold theorem for surfaces (7) an the surface Gaussian theorem 13. Using again the condition that this equation holds for all legal subsurfaces $\sigma \in \Sigma$ one obtains the **local equation of balance for singular surfaces**

$$\frac{\partial\, \underset{\mathrm{s}}{a}(\mathbf{x},t)}{\partial\, t} = -\underset{\mathrm{s}}{\mathrm{div}}\,(\underset{\mathrm{s}}{a}(\mathbf{x},t)\underset{\mathrm{s}}{\mathbf{v}} + \underset{\mathrm{s}}{\mathbf{j}_a}) - \kappa\, \underset{\mathrm{s}}{a}(\mathbf{x},t)\, v_n + \underset{\mathrm{s}}{r_a}(\mathbf{x},t) \quad \forall \mathbf{x} \in \Sigma. \tag{1.150}$$

1.2.3 Volume balance equations containing singular surfaces

Next, consider a volume $\Omega = \Omega^+ \cup \Omega^-$ with $\Omega^+ \cap \Omega^- = \Sigma$ and $\partial\,\Omega^+ = \Sigma^+ \cup \Sigma$, $\partial\Omega^- = \Sigma^- \cup \Sigma$.

For any subvolume ω which is either completely in Ω^+ or Ω^-, the local balance equation (1.147) holds. Subvolumes which intersect Σ obey at the interface some jump conditions which will now be derived. It is convenient to introduce the jump brackets $[\![\cdot]\!]$ for a property $a(\mathbf{x},t)$, $\mathbf{x} \in \Sigma$ where $\mathbf{n}$ denotes the outward normal of Σ (here, pointing into

Ω^+),

$$[\![a(\mathbf{x},t)]\!] := a^+(\mathbf{x},t) - a^-(\mathbf{x},t) \qquad \mathbf{x} \in \Sigma \tag{1.151}$$

$$a^+(\mathbf{x},t) := \lim_{h\to 0} a(\mathbf{x} + h\cdot\mathbf{n},t) \qquad \mathbf{x} + h\cdot\mathbf{n} \in \Omega^+ \tag{1.152}$$

$$a^-(\mathbf{x},t) := \lim_{h\to 0} a(\mathbf{x} - h\cdot\mathbf{n},t) \qquad \mathbf{x} - h\cdot\mathbf{n} \in \Omega^-. \tag{1.153}$$

Quite similar to the alternative definition of a surface property via a shrinking volume element (*c.f.* page 21) the jump conditions will be derived with a pillbox argument[5]. Consider a volume element $\omega = \omega^+ \cup \omega^-$, $\omega^+ \in \Omega^+$, $\omega^- \in \Omega^-$ which is an orthogonal extension of a surface element $\sigma \in \Sigma$ into Ω^+ and Ω^-, namely the pillbox

$$\mathbf{p}(u,v,w) = \mathbf{p}_A(u,v) + h\cdot w\mathbf{n} \quad (u,v) \in S, w \in [-1,1] \tag{1.154}$$

with $\mathbf{p}_A(S) = \sigma$ and $\mathbf{p}(S\times[-1,1]) = \omega$. According to the definition of the pillbox, the boundary $\partial\omega$ could further decomposed into the parallel components $\sigma^\pm := \sigma \pm h\mathbf{n}$ and the skin surface $\sigma_h := \partial\sigma + [-h,h]\mathbf{n}$ with

$$\lim_{h\to 0} \sigma^\pm = \sigma \tag{1.155}$$

$$\lim_{h\to 0} \sigma_h = \partial\sigma. \tag{1.156}$$

Note that for $\mathbf{p}_C(L) = \partial\sigma$ the skin surface is parametrized via

$$\mathbf{p}(v,w) = \mathbf{p}_L(v) + h\cdot w\mathbf{n} \quad v \in L, w \in [-1,1]. \tag{1.157}$$

The (global) balance equation for the volume element ω is hence

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_\omega a(\mathbf{x},t)\,dV + \frac{\mathrm{d}}{\mathrm{d}t}\int_\sigma \underset{\mathrm{s}}{a}(\mathbf{x},t)\,dA(\mathbf{x}) &= \int_\omega r_a(\mathbf{x},t)\,dV - \oint_{\partial\omega} \mathbf{j}_a^{\mathrm{T}}\cdot\,d\mathbf{A}(\mathbf{x}) \\ &\quad + \int_\sigma \underset{\mathrm{s}}{r_a}(\mathbf{x},t) - \underset{\mathrm{s}}{\mathrm{div}}\,\underset{\mathrm{s}}{\mathbf{j}_a}\,dA(\mathbf{x}).\end{aligned} \tag{1.158}$$

Next, the limit $h \to 0$ is carried out. For the first part of the left hand side one deduces

$$\lim_{h\to 0}\frac{\mathrm{d}}{\mathrm{d}t}\int_\omega a(\mathbf{x},t)\,dV = \lim_{h\to 0}\left(\int_\omega \frac{\partial a}{\partial t}\,dV + \oint_{\partial\omega} a\mathbf{v}^{\mathrm{T}}\cdot\,d\mathbf{A}\right) \tag{1.159}$$

$$= \int_\sigma [\![a(\mathbf{x},t)\mathbf{v}^{\mathrm{T}}(\mathbf{x},t)]\!]\cdot\mathbf{n}\,dA \tag{1.160}$$

according to the auxiliary calculations 1.9 and 1.10. Similar calculations show

$$\lim_{h\to 0}\left(\int_\omega r_a(\mathbf{x},t)\,dV - \oint_{\partial\omega}\mathbf{j}_a^{\mathrm{T}}\cdot\,d\mathbf{A}(\mathbf{x})\right) = -\int_\sigma [\![\mathbf{j}_a^{\mathrm{T}}]\!]\cdot\mathbf{n}\,dA \tag{1.161}$$

and thus finally

$$\int_\sigma \left(\frac{\partial \underset{\mathrm{s}}{a}}{\partial t} + \underset{\mathrm{s}}{\operatorname{div}} \left(\underset{\mathrm{s}}{a}\, \underset{\mathrm{s}}{\mathbf{v}} + \underset{\mathrm{s}}{\mathbf{j}_a}\right) + \kappa\, \underset{\mathrm{s}}{a} v_n + [\![a\mathbf{v}^{\mathrm{T}} + \mathbf{j}_a^{\mathrm{T}}]\!] \cdot \mathbf{n} - \underset{\mathrm{s}}{r_a} \right) dA = 0. \tag{1.162}$$

Again, this equation is supposed to hold for every $\sigma \in \Sigma$ and thus the **local surface balance with jump conditions** is obtained,

$$\frac{\partial \underset{\mathrm{s}}{a}}{\partial t} = -\underset{\mathrm{s}}{\operatorname{div}} \left(\underset{\mathrm{s}}{a}\, \underset{\mathrm{s}}{\mathbf{v}} + \underset{\mathrm{s}}{\mathbf{j}_a}\right) - \kappa\, \underset{\mathrm{s}}{a} v_n + \underset{\mathrm{s}}{r_a} - [\![a\mathbf{v}^{\mathrm{T}} + \mathbf{j}_a^{\mathrm{T}}]\!] \cdot \mathbf{n} \qquad \forall \mathbf{x} \in \Sigma. \tag{1.163}$$

Auxiliary calculation 1.9:

$$\begin{aligned}
&\lim_{h\to 0} \int_\omega \frac{\partial\, a(\mathbf{x},t)}{\partial t}\, dV \\
&= \lim_{h\to 0} \int_{-1}^{1} \iint_S \frac{\partial\, a(\mathbf{p}(u,v,w),t)}{\partial t} \left| \left\langle \frac{\partial \mathbf{p}}{\partial w}, \left(\frac{\partial \mathbf{p}}{\partial u} \times \frac{\partial \mathbf{p}}{\partial v} \right) \right\rangle \right| d(u,v,w) \\
&= \int_{-1}^{1} \iint_S \lim_{h\to 0} h \left(\underbrace{\frac{\partial\, a(\underset{\mathrm{s}}{\mathbf{p}} + h\cdot w\mathbf{n},t)}{\partial t}}_{<\infty} \underbrace{\left| \left\langle \mathbf{n}, \left(\frac{\partial \underset{\mathrm{s}}{\mathbf{p}}}{\partial u} \times \frac{\partial \underset{\mathrm{s}}{\mathbf{p}}}{\partial v} \right) \right\rangle \right|}_{<\infty} \right) d(u,v,w) = 0
\end{aligned}$$

Auxiliary calculation 1.10:

$$\begin{aligned}
&\lim_{h\to 0} \oint_{\partial\omega} a(\mathbf{x},t)\mathbf{v}(\mathbf{x},t) \cdot d\mathbf{A} \\
&= \lim_{h\to 0} \left(\int_{\sigma^+} a(\mathbf{x},t)\mathbf{v}(\mathbf{x},t) \cdot d\mathbf{A} - \int_{\sigma^-} a(\mathbf{x},t)\mathbf{v}(\mathbf{x},t) \cdot d\mathbf{A} + \int_{\sigma_h} a(\mathbf{x},t)\mathbf{v}(\mathbf{x},t) \cdot d\mathbf{A} \right) \\
&= \lim_{h\to 0} \iint_S a(\underset{\mathrm{s}}{\mathbf{p}} + h\cdot\mathbf{n},t)\mathbf{v}^{\mathrm{T}}(\underset{\mathrm{s}}{\mathbf{p}} + h\cdot\mathbf{n},t) \cdot \left(\frac{\partial \underset{\mathrm{s}}{\mathbf{p}}}{\partial u} \times \frac{\partial \underset{\mathrm{s}}{\mathbf{p}}}{\partial v} \right) d(u,v) \\
&- \lim_{h\to 0} \iint_S a(\underset{\mathrm{s}}{\mathbf{p}} - h\cdot\mathbf{n},t)\mathbf{v}^{\mathrm{T}}(\underset{\mathrm{s}}{\mathbf{p}} - h\cdot\mathbf{n},t) \cdot \left(\frac{\partial \underset{\mathrm{s}}{\mathbf{p}}}{\partial u} \times \frac{\partial \underset{\mathrm{s}}{\mathbf{p}}}{\partial v} \right) d(u,v) \\
&+ \lim_{h\to 0} h \cdot \left(\underbrace{\int_{-1}^{1} \int_L a(\mathbf{p}_b(v) + hw\mathbf{n},t)\mathbf{v}^{\mathrm{T}}(\mathbf{p}_b(v) + hw\mathbf{n},t) \left(\frac{\partial \mathbf{p}_b}{\partial v} \times \mathbf{n} \right) d(v,w)}_{<\infty} \right) \\
&= \int_\sigma a^+(\mathbf{x},t)\mathbf{v}^+(\mathbf{x},t) - a^-(\mathbf{x},t)\mathbf{v}^-(\mathbf{x},t)\, d\mathbf{A} = \int_\sigma [\![a\mathbf{v}]\!] \cdot \mathbf{n}\, dA
\end{aligned}$$

Note the minus sign in front of $\int_{\sigma^-} a\mathbf{v}^{\mathrm{T}}\, d\mathbf{A}$ due to the orientation of σ^-.

Flux Balance equations

Reynolds transport theorem for second kind surface integrals states

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Sigma}\mathbf{c}^{\mathrm{T}}(\mathbf{x},t)\cdot d\mathbf{A}=\int\limits_{\Sigma}\left(\frac{\partial\,\mathbf{c}(\mathbf{x},t)}{\partial\,t}+(\operatorname{div}\mathbf{c})\cdot\mathbf{v}(\mathbf{x},t)\right)^{\mathrm{T}}\cdot d\mathbf{A}(\mathbf{x}) \tag{1.164}$$

$$+\oint\limits_{\partial\Sigma}(\mathbf{c}(\mathbf{x},t)\times\mathbf{v}(\mathbf{x},t))^{\mathrm{T}}\cdot d\mathbf{s}(\mathbf{x}). \tag{1.165}$$

Hence, the global equation of balance for flux density $\mathbf{c}$ reads

$$\int\limits_{\Sigma}\frac{\partial\,\mathbf{c}^{\mathrm{T}}(\mathbf{x},t)}{\partial\,t}\cdot d\mathbf{A}=-\int\limits_{\Sigma}((\operatorname{div}\mathbf{c}(\mathbf{x},t))\cdot\mathbf{v}(\mathbf{x},t)-\mathbf{r}_{\mathbf{c}}(\mathbf{x},t))^{\mathrm{T}}\cdot d\mathbf{A}$$

$$-\int\limits_{\partial\Sigma}(\mathbf{j}_{\mathbf{c}}(\mathbf{x},t)+\mathbf{c}(\mathbf{x},t)\times\mathbf{v}(\mathbf{x},t))^{\mathrm{T}}\cdot d\mathbf{s}. \tag{1.166}$$

Applying the Kelvin–Stokes theorem leads to the **local balance equation of flux properties**

$$\frac{\partial\,\mathbf{c}(\mathbf{x},t)}{\partial\,t}=-\operatorname{curl}(\mathbf{j}_{\mathbf{c}}(\mathbf{x},t)+\mathbf{c}(\mathbf{x},t)\times\mathbf{v}(\mathbf{x},t))-(\operatorname{div}\mathbf{c})\cdot\mathbf{v}(\mathbf{x},t)+\mathbf{r}_{\mathbf{c}}(\mathbf{x},t). \tag{1.167}$$

If this equation is supposed to hold for every arbitrary $\omega\in\Omega$ it is the resulting local balance equation.

Flux balance equations containing singular lines

If the surface $\Sigma=\mathbf{p}_A(S)$ is divided into two parts Σ^+ and Σ^- by a line[2] $\Psi=\mathbf{p}_C(L)$, similar to the pillbox in the volume a pipe of width h around a curve $\psi\subset\Psi$ could be built. For a given point $\mathbf{x}_0\in\psi$ there exist $(u_0,v_0)\in S$ and $w_0\in L$ with

$$\mathbf{x}_0=\mathbf{p}_C(w_0)=\mathbf{p}_A(u_0,v_0) \tag{1.168}$$

$$\mathbf{t}=\frac{\partial\,\mathbf{p}_C(w)}{\partial\,w}\Big|_{w=w_0}\in T_{\mathbf{x}_0}(\Sigma) \tag{1.169}$$

$$\mathbf{n}=\frac{\frac{\partial\,\mathbf{p}_A(u,v)}{\partial\,u}\times\frac{\partial\,\mathbf{p}_A(u,v)}{\partial\,v}}{\left|\left|\frac{\partial\,\mathbf{p}_A(u,v)}{\partial\,u}\times\frac{\partial\,\mathbf{p}_A(u,v)}{\partial\,v}\right|\right|}\Bigg|_{(u,v)=(u_0,v_0)}\in N_{\mathbf{x}_0} \tag{1.170}$$

$$\mathbf{b}:=\frac{\mathbf{t}\times\mathbf{n}}{||\mathbf{t}\times\mathbf{n}||} \tag{1.171}$$

$$T_{\mathbf{x}_0}=\operatorname{span}\{\mathbf{t},\mathbf{b}\} \tag{1.172}$$

Consider small domain $\sigma=\sigma^+\cup\sigma^-\in\Sigma$ such that[3]

$$\mathbf{p}(u,v)=\mathbf{p}_L(u)+h\cdot v\,\mathbf{t}\times\mathbf{n}\quad(u,v)\in S' \tag{1.173}$$

$$\mathbf{p}(S')=\sigma \tag{1.174}$$

[2] in general this line is obtained by intersecting two surfaces.
[3] The domain is chosen small enough to ensure $\mathbf{n}=$ const. and $\mathbf{t}=$ const.

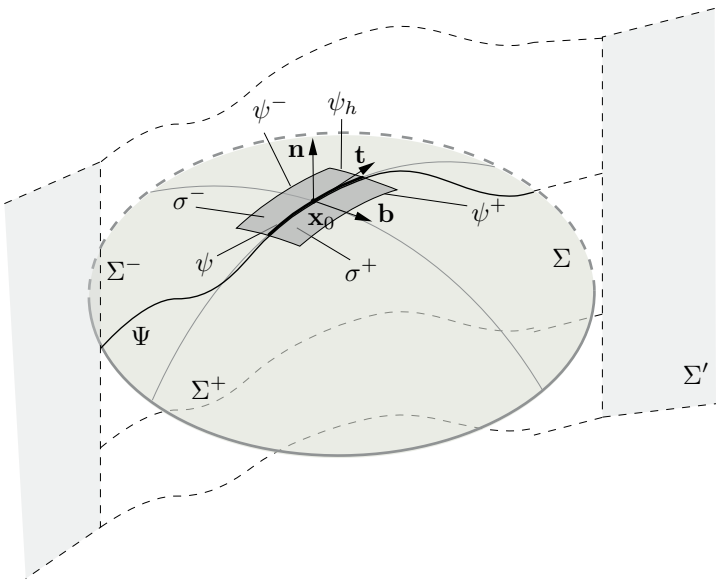

Figure 1.7.: Sketch of a 2-D pillbox $\sigma = \sigma^+ \cup \sigma^-$ on a surface Σ. At a fixed point $\mathbf{x}_0$ the tupel $(\mathbf{n}, \mathbf{t}, \mathbf{b})$ is the Frenet–Serret frame with the normal vector $\mathbf{n}$, the tangent vector $\mathbf{t}$ and the binormal vector $\mathbf{b}$. The surface curve Ψ is obtained from intersecting Σ with another surface Σ'.

and with boundary components $\partial\sigma = \psi^+ \cup \psi^- \cup \psi_h$ such that

$$\lim_{h\to 0} \psi^{\pm} = \psi \tag{1.175}$$

$$\lim_{h\to 0} \psi_h = \partial\psi. \tag{1.176}$$

The jump bracket on the surface is defined analogous, but instead of $\mathbf{n}$ as pointer the binormal vector $\mathbf{b}$ is used, *i.e.*

$$[\![\mathbf{c}(\mathbf{x},t)]\!] := \mathbf{c}^+(\mathbf{x},t) - \mathbf{c}^-(\mathbf{x},t) \qquad \mathbf{x} \in \Psi \tag{1.177}$$

$$\mathbf{c}^+(\mathbf{x},t) := \lim_{h\to 0} \mathbf{c}(\mathbf{x} + h\cdot\mathbf{b}, t) \qquad \mathbf{x} + h\cdot\mathbf{b} \in \Sigma^+ \tag{1.178}$$

$$\mathbf{c}^-(\mathbf{x},t) := \lim_{h\to 0} \mathbf{c}(\mathbf{x} - h\cdot\mathbf{b}, t) \qquad \mathbf{x} - h\cdot\mathbf{b} \in \Sigma^-. \tag{1.179}$$

Again, the local balance equation for points on the curve Ψ are obtained from the global balance equation for $\sigma = \sigma^+ \cup \sigma^-$, $\psi = \sigma^+ \cup \sigma^-$ and $h \to 0$, *i.e.*

$$\begin{aligned}\lim_{h\to 0} \int_{\sigma} \frac{\partial\, \mathbf{c}^{\mathrm{T}}(\mathbf{x},t)}{\partial\, t} \cdot d\mathbf{A} = &- \lim_{h\to 0} \int_{\sigma} \left((\operatorname{div} \mathbf{c}(\mathbf{x},t)) \cdot \mathbf{v}(\mathbf{x},t) - \mathbf{r}_{\mathbf{c}}(\mathbf{x},t)\right)^{\mathrm{T}} \cdot d\mathbf{A} \\ &- \lim_{h\to 0} \int_{\partial\sigma} \left(\mathbf{j}_{\mathbf{c}}(\mathbf{x},t) + \mathbf{c}(\mathbf{x},t) \times \mathbf{v}(\mathbf{x},t)\right)^{\mathrm{T}} \cdot d\mathbf{s} \\ &+ \int_{\psi} \mathbf{r}_{\mathbf{c}}^{\mathrm{T}}(\mathbf{x},t) \cdot d\mathbf{s}.\end{aligned} \tag{1.180}$$

Similar to the pillbox limit in the volume, all contributions from surface properties

vanish, *i.e.*

$$\lim_{h\to 0}\int_{\sigma} \frac{\partial\, \mathbf{c}^{\mathrm{T}}(\mathbf{x},t)}{\partial\, t} \cdot d\mathbf{A} = 0 \tag{1.181}$$

$$\lim_{h\to 0}\int_{\sigma} \left((\operatorname{div}\mathbf{c}(\mathbf{x},t)) \cdot \mathbf{v}(\mathbf{x},t) - \mathbf{r}_{\mathbf{c}}(\mathbf{x},t)\right)^{\mathrm{T}} \cdot d\mathbf{A} = 0. \tag{1.182}$$

Together with the auxiliary calculation 1.11 and the assumption that equation (1.180) holds for every $\psi \subset \Psi$ the **jump conditions for vector fields on singular points**

$$[\![\mathbf{j}_{\mathbf{c}}(\mathbf{x},t) + \mathbf{c}(\mathbf{x},t) \times \mathbf{v}(\mathbf{x},t)]\!] = \underset{\mathrm{s}}{\mathbf{r}_{\mathbf{c}}}(\mathbf{x},t) \quad \forall \mathbf{x} \in \Psi \tag{1.183}$$

are obtained.

Auxiliary calculation 1.11:

$$\begin{aligned}
&\lim_{h\to 0}\int_{\partial\sigma} \left(\mathbf{j}_{\mathbf{c}}(\mathbf{x},t) + \mathbf{c}(\mathbf{x},t) \times \mathbf{v}(\mathbf{x},t)\right)^{\mathrm{T}} \cdot d\mathbf{s} \\
&= \lim_{h\to 0}\int_{\psi} \left(\mathbf{j}_{\mathbf{c}}(\mathbf{x}+h\mathbf{n},t) + \mathbf{c}(\mathbf{x}+h\mathbf{n},t) \times \mathbf{v}(\mathbf{x}+h\mathbf{n},t)\right)^{\mathrm{T}} \cdot d\mathbf{s} \\
&\quad - \lim_{h\to 0}\int_{\psi} \left(\mathbf{j}_{\mathbf{c}}(\mathbf{x}-h\mathbf{b},t) + \mathbf{c}(\mathbf{x}-h\mathbf{b},t) \times \mathbf{v}(\mathbf{x}-h\mathbf{b},t)\right)^{\mathrm{T}} \cdot d\mathbf{s} \\
&\quad + \lim_{h\to 0}\int_{\psi_h} \left(\mathbf{j}_{\mathbf{c}}(\mathbf{x},t) + \mathbf{c}(\mathbf{x},t) \times \mathbf{v}(\mathbf{x},t)\right)^{\mathrm{T}} \cdot d\mathbf{s} \\
&\quad = \int_{\sigma} [\![\mathbf{j}_{\mathbf{c}}(\mathbf{x},t) + \mathbf{c}(\mathbf{x},t) \times \mathbf{v}(\mathbf{x},t)]\!]^{\mathrm{T}} \cdot d\mathbf{s}
\end{aligned}$$

1.2.4 Summary balance equations

In the proceeding chapter local balance equations were derived via transport theorems and global balance equations. Volume elements containing a singular surface obey some jump conditions which were derived from a pillbox argument. Of course, a tensorial extension of the derived local balance equations is possible, and also necessary for the momentum balance. It is again a straight forward extension according to the definitions in section 1.1.1. In the next section coordinate transformations are carried out to derive the equivalent balance equations in various frames of reference.

1.3 Coordinate transformations

For the description of a physical object a variety of useful frames of references exist. Nevertheless, inertial frames of reference are desired since Newton's law of inertia holds in its simplest form, or in other words, no fictitious forces are present. Two inertial (or Galilean) frames of reference are related by a Galilei-transformation $T_G^0 : \Omega_0 \times I \to \Omega_{\mathbf{x}}(t) \subset \mathbb{R}^3 \times I$ with

$$(\boldsymbol{\xi}, \tau) \mapsto (\mathbf{A} \cdot \boldsymbol{\xi} + \mathbf{v}' \cdot \tau, \tau) = (\mathbf{x}, \tau). \tag{1.184}$$

It describes the coordinate transformation due to translation (with respect to some constant velocity field $\mathbf{v}$) and some rotation (with rotational matrix $\mathbf{A}$) of $\boldsymbol{\xi}$ to $\mathbf{x}$. The Galilei transformation could be generalized for a velocity field, *i.e.* a space dependent property $\mathbf{v}(\boldsymbol{\xi})$, which leads to $T_G : \Omega_0 \times I \to \Omega_{\mathbf{x}}(t) \times I$ with

$$(\boldsymbol{\xi}, t) \mapsto (\mathbf{A} \cdot \boldsymbol{\xi} + \mathbf{v}'(\boldsymbol{\xi}) \cdot t, t) = (\mathbf{x}, t) \tag{1.185}$$

This is still a Galilei transformation as the velocity field is assumed to be constant with respect to time; nevertheless the $\mathbf{v}$ is a field.
Of course, when electrodynamics comes into play or when the velocity $\mathbf{v}$ is close to speed of light c_0 the group of Galilei-transformations is not anymore the one which transforms inertial systems onto each other. However, the Lorentz-transformation $T_L^0 : \Omega_0 \times I \to \Omega_{\mathbf{x}}(t) \subset \mathbb{R}^3 \times I$ with

$$(\boldsymbol{\xi}, \tau) \mapsto (\mathbf{A} \cdot \boldsymbol{\xi} + \gamma\, \mathbf{v}' \cdot \tau + (\gamma - 1) \frac{\langle \boldsymbol{\xi}, \mathbf{v}' \rangle}{||\mathbf{v}||^2} \cdot \mathbf{v}', \gamma\, \tau + \frac{1 - \gamma^2}{\gamma} \frac{\langle \boldsymbol{\xi}, \mathbf{v}' \rangle}{||\mathbf{v}||^2}) = (\mathbf{x}, t) \tag{1.186}$$

takes this function and thus substitutes the Galilei-transformation. Clearly, for $\gamma \to 1$ the Lorentz-transformation is approaching the Galilei-transformation. For the sake of simplicity I rely on Galilei-transformations, while knowing that the actual Maxwell's equations are only invariant under Lorentz-transformations. Whenever relativistic effects are crucial it will be discussed at that position.

After a brief introduction on Eulerian and Lagrangian coordinates a derivation of the transformation laws[6] between Lagrangian and Eulerian as well as between two Eulerian coordinate systems will given in this section.

1.3.1 Transformation between Eulerian and Lagrangian coordinates

Consider the *initial* domain $\Omega_0 \in \mathbb{R}^3$ with space coordinates $\boldsymbol{\xi} \in \Omega_0$ and consider an arbitrary velocity field $\hat{\mathbf{v}}_{\mathbf{x}}(\boldsymbol{\xi})$, describing the motion of *observers*[4], or simply, a fluid. The corresponding Galilei-transformation is thus $T_G : \Omega_0 \times I \to \Omega_{\mathbf{x}}(t) \subset \mathbb{R}^3 \times I$ with $(\boldsymbol{\xi}, t) \mapsto (\boldsymbol{\xi} + \hat{\mathbf{v}}_{\mathbf{x}}(\boldsymbol{\xi}) \cdot t, t) = (\mathbf{x}, t)$. However, a general coordinate transformation for a

[4]The term observer is used here to emphasises that one knows the actual velocity field without interacting with the field itself.

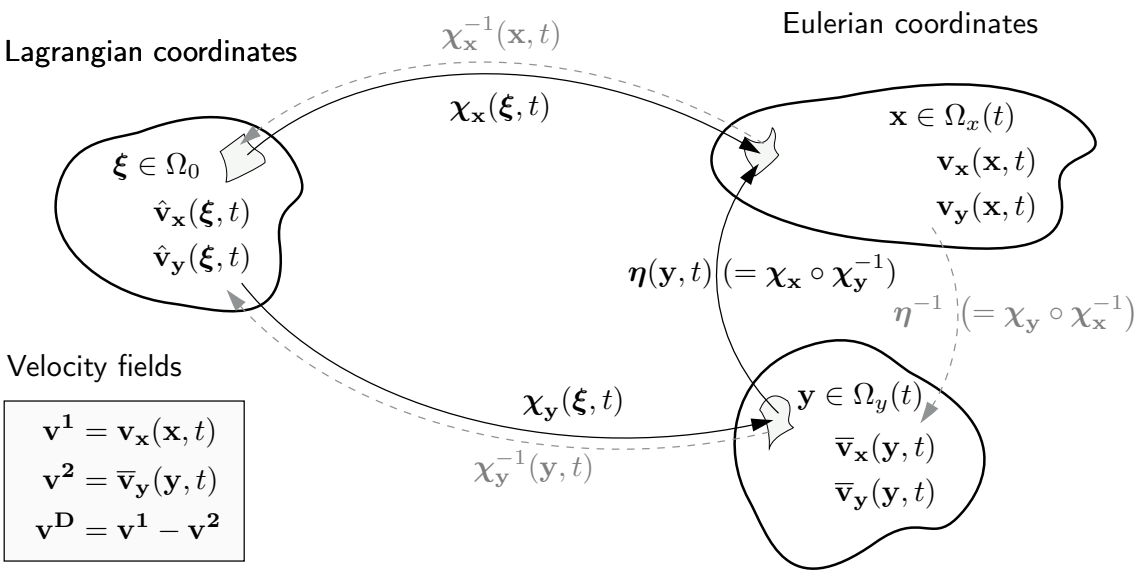

Figure 1.8.: Description of Lagrangian and Eulerian coordinates with two different *material* velocities $\mathbf{v_x}$ and $\mathbf{v_y}$ (and their corresponding coordinates $\mathbf{x}$ and $\mathbf{y}$).

given, transient velocity field $\hat{\mathbf{v}}_{\mathbf{x}}(\boldsymbol{\xi},t)$ is hence a map[5]

$$T : \Omega_0 \times I \to \Omega_{\mathbf{x}}(t) \subset \mathbb{R}^3 \times I \tag{1.187}$$

$$(\boldsymbol{\xi},t) \mapsto T(\boldsymbol{\xi},t) = (\underbrace{\boldsymbol{\xi} + \int_{t_0}^{t} \hat{\mathbf{v}}_{\mathbf{x}}(\boldsymbol{\xi},\tau)\mathrm{d}\tau}_{=\chi_{\mathbf{x}}(\boldsymbol{\xi},t;t_0)}, t) = (\mathbf{x},t) \tag{1.188}$$

and $\chi_{\mathbf{x}}(\boldsymbol{\xi},t;t_0)$ is called motion. Since t_0 is always chosen as reference or initial time, $t_0 = 0$, the motion will be abbreviated as $\chi_{\mathbf{x}}(\boldsymbol{\xi},t)$. The pair $(\boldsymbol{\xi},t)$ are called **Lagrangian coordinates** (often in literature also material coordinate). Clearly the velocity field $\hat{\mathbf{v}}_{\mathbf{x}}$ coincides with the temporal derivative of the motion, *i.e.*

$$\frac{\partial \chi_{\mathbf{x}}(\boldsymbol{\xi},t)}{\partial t} = \hat{\mathbf{v}}(\boldsymbol{\xi},t). \tag{1.189}$$

The *velocity field of the observer* is yet undetermined. A variety of *useful* velocity fields for an observer are imaginable, *e.g.*

- the barycentric velocity $\mathbf{v}^M$, obtained from a mass flux
- the electric drift velocity $\mathbf{v}^C$, obtained from the electric current
- or just an arbitrary velocity field.

Let exemplarily $\mathbf{v}^1$ be an arbitrary observer velocity field. If $\mathbf{v^1}$ could be expressed in

[5]Of course, even more general transformations are considerable, *e.g.*

$$(\boldsymbol{\xi},t) \mapsto T(\boldsymbol{\xi},t) = (\mathbf{A} \cdot \boldsymbol{\xi} + \int_{t_0}^{t} \hat{\mathbf{v}}_{\mathbf{x}}(\boldsymbol{\xi},\tau)\mathrm{d}\tau, t),$$

but within this work the simplified transformation (1.187) is satisfactory.

terms of the Lagrangian coordinates as

$$\mathbf{v^1} = \hat{\mathbf{v}}_{\mathbf{x}}(\boldsymbol{\xi}, t) \tag{1.190}$$

it serves thus for the general coordinate transformation (1.187).

Possibly an explicit expression (or relationship to other physical properties) of the velocity field $\hat{\mathbf{v}}_{\mathbf{x}}(\boldsymbol{\xi}, t)$ in the Lagrangian coordinates $(\boldsymbol{\xi}, t)$ is not elementarily accessible. However, if a coordinate system $\mathbf{x} \in \Omega_{\mathbf{x}}(t)$ is chosen such that an explicit expression of $\mathbf{v^1}$ is possible,

$$\mathbf{v^1} = \mathbf{v}_{\mathbf{x}}(\mathbf{x}, t), \tag{1.191}$$

it is termed **Eulerian coordinate system**. One could also say that the Eulerian coordinate system is implicitly defined via the explicit representation of $\mathbf{v^1}$ in $(\mathbf{x}, t)$. Similar to the diffeomorphism $T : \Omega_0 \times I \to \Omega_{\mathbf{x}}(t) \times I$ an inverse coordinate transformation is thus declared due to

$$T^{-1} : \Omega_{\mathbf{x}}(t) \times I \to \Omega_0 \subset \times I \tag{1.192}$$

$$(\mathbf{x}, t) \mapsto T_{\mathbf{x}}^{-1}(\mathbf{x}, t) = (\underbrace{\mathbf{x} - \int_{t_0}^{t} \mathbf{v}_{\mathbf{x}}(\mathbf{x}, \tau)\mathrm{d}\tau}_{=\chi_{\mathbf{x}}^{-1}(\mathbf{x}, t; t_0)}, t) = (\boldsymbol{\xi}, t), \tag{1.193}$$

if Ω_0 and $\Omega_{\mathbf{x}}(t)$ coincide at $t_0 = 0$. Since the velocity is independent of the actual description in any coordinate system

$$\mathbf{v^1} = \hat{\mathbf{v}}_{\mathbf{x}}(\boldsymbol{\xi}, t) = \mathbf{v}_{\mathbf{x}}(\mathbf{x}, t), \tag{1.194}$$

and with with eq. (1.187) one concludes

$$\hat{\mathbf{v}}_{\mathbf{x}}(\boldsymbol{\xi}, t) = \mathbf{v}_{\mathbf{x}}(\boldsymbol{\chi}_{\mathbf{x}}(\boldsymbol{\xi}, t), t). \tag{1.195}$$

It is thus shown that $\mathbf{v}_{\mathbf{x}}$ is actually a **material velocity**.

Extensive properties in Eulerian and Lagrangian coordinates

Let $A(t)$ be global extensive properties with its corresponding field $a(\mathbf{x}, t)$, *i.e.*

$$A(t) = \int_{\Omega_{\mathbf{x}}(t)} a(\mathbf{x}, t)\, dV(\mathbf{x}) \tag{1.196}$$

The density property $a(\mathbf{x}, t)$ is called **Eulerian density** of the macroscopic properties $A(t)$[6]. According to the volume integral transformation the macroscopic properties can also be expressed in Lagrangian coordinates,

$$A(t) = \int_{\Omega_{\mathbf{x}}(t)} a(\mathbf{x}, t)\, dV(\mathbf{x}) = \int_{\Omega_0} a(\boldsymbol{\chi}_{\mathbf{x}}(\boldsymbol{\xi}, t), t) \det\left(\mathbf{F}(\boldsymbol{\xi}, t)\right)\, d\hat{V}(\boldsymbol{\xi}) \tag{1.197}$$

$$= \int_{\Omega_0} \hat{a}(\boldsymbol{\xi}, t)\, d\hat{V}(\boldsymbol{\xi}) \tag{1.198}$$

[6] A similar derivation holds for vector valued properties $\vec{B}(t)$.

and

$$\hat{a}(\boldsymbol{\xi}, t) := J(\boldsymbol{\xi}, t) \cdot a(\boldsymbol{\chi}_{\mathbf{x}}(\boldsymbol{\xi}, t), t) \tag{1.199}$$

$$J(\boldsymbol{\xi}, t) := \det\left(\mathbf{F}(\boldsymbol{\xi}, t)\right) \tag{1.200}$$

is called **Lagrangian density** of A. The matrix $\mathbf{F}(\boldsymbol{\xi}, t)$, called **deformation gradient**, is the jacobian of the transformation $\boldsymbol{\chi}_{\mathbf{x}}$ between the Eulerian and Lagrangian coordinates, *i.e.* $\mathbf{F}(\boldsymbol{\xi}, t) = \boldsymbol{\nabla}\boldsymbol{\chi}_{\mathbf{x}}(\boldsymbol{\xi}, t)$. Note, however, that it is in general difficult to obtain the explicit representation of $\boldsymbol{\chi}_{\mathbf{x}}$.

Fluxes in Eulerian and Lagrangian coordinates

Let $\Phi_a(t)$ be the (global) fluxes of some flux densities $\mathbf{j}_a(\mathbf{x}, t)$, *i.e.*

$$\Phi_a = \int\limits_{\partial\Omega_{\mathbf{x}}(t)} \mathbf{j}_a(\mathbf{x}, t)^{\mathrm{T}} \cdot d\mathbf{A}(\mathbf{x}). \tag{1.201}$$

Then $\mathbf{j}_a(\mathbf{x}, t)$ is similarly called **Eulerian flux density**. Naturally the surface integral transformation (*c.f.* theorem 1) is used to deduce

$$\Phi_a = \int\limits_{\partial\Omega_{\mathbf{x}}(t)} \mathbf{j}_a(\mathbf{x}, t)^{\mathrm{T}} \cdot d\mathbf{A}(\mathbf{x}) \tag{1.202}$$

$$= \int\limits_{\partial\Omega_0} J \cdot \mathbf{j}_a^{\mathrm{T}} \cdot \mathbf{F}^{-\mathrm{T}} \cdot d\hat{\mathbf{A}}(\boldsymbol{\xi}) \tag{1.203}$$

and thus the **Lagrangian flux**

$$\hat{\mathbf{j}}_a(\boldsymbol{\xi}, t) := J(\boldsymbol{\xi}, t)\mathbf{F}^{-1}(\boldsymbol{\xi}, t) \cdot \mathbf{j}_a(\boldsymbol{\chi}_{\mathbf{x}}(\boldsymbol{\xi}, t), t). \tag{1.204}$$

However, applying the divergence theorem on eq. 1.202 and 1.203 leads to the **divergence transformation**

$$J \cdot \mathrm{div}_{\mathbf{x}}\, \mathbf{j}_a = \mathrm{div}_{\boldsymbol{\xi}} \left(J \cdot \mathbf{F}^{-1}\mathbf{j}_a\right) = \mathrm{div}_{\boldsymbol{\xi}}\, \hat{\mathbf{j}}_a. \tag{1.205}$$

Time derivative of extensive properties

Next, the evolution of global extensive properties, expressed in either Eulerian or Lagrangian coordinates is investigated and a relationship between the local evolution equations derived. Consider again the extensive properties $A(t)$ and $\vec{B}(t)$ with their respective Eulerian densities $a(\mathbf{x}, t)$ and $\mathbf{b}(\mathbf{x}, t)$. Then, according to Reynolds transport theorem for volume integrals,

$$\frac{\mathrm{d}\,A(t)}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t} \int\limits_{\Omega_{\mathbf{x}}(t)} a(\mathbf{x}, t)\, dV(\mathbf{x}) \tag{1.206}$$

$$= \int\limits_{\Omega_{\mathbf{x}}(t)} \frac{\partial\, a(\mathbf{x}, t)}{\partial\, t} + \mathrm{div}\left(a(\mathbf{x}, t) \cdot \mathbf{v}(\mathbf{x}, t)\right) dV(\mathbf{x}) \tag{1.207}$$

$$= \int\limits_{\Omega_0} \frac{\partial\, \hat{a}(\boldsymbol{\xi}, t)}{\partial\, t}\, d\hat{V}(\boldsymbol{\xi}), \tag{1.208}$$

leading to the (local) time derivative transformation

$$J \cdot \left(\frac{\partial\, a(\mathbf{x},t)}{\partial\, t} + \operatorname{div}\left(a(\mathbf{x},t) \cdot \mathbf{v}(\mathbf{x},t)\right) dV(\mathbf{x}) \right) = \frac{\partial\, \hat{a}(\boldsymbol{\xi},t)}{\partial\, t}. \tag{1.209}$$

Transformation of local balance equations

With the above transformation laws for densities and fluxes the equivalent local balance law in Lagrangian coordinates is derived. Assume a local balance law according to equation 1.147, *i.e.*

$$\frac{\partial\, a(\mathbf{x},t)}{\partial\, t} = -\operatorname{div}_{\mathbf{x}}\left(a \cdot \mathbf{v} + \mathbf{j}_a\right) + r_a \quad \mathbf{x} \in \Omega_{\mathbf{x}}(t). \tag{1.210}$$

The corresponding **local balance equation in Lagrangian coordinates**[7] is hence

$$\frac{\partial\, \hat{a}(\boldsymbol{\xi},t)}{\partial\, t} = -\operatorname{div}_{\boldsymbol{\xi}} \hat{\mathbf{j}}_a(\boldsymbol{\xi},t) + \hat{r}(\boldsymbol{\xi},t) \tag{1.211}$$

with $\boldsymbol{\xi} = \boldsymbol{\chi}_{\mathbf{x}}^{-1}(\mathbf{x},t)$ and since $J \neq 0\ \forall(\boldsymbol{\xi},t)$. The eulerian description is certainly useful when $J \equiv 1$ (incompressibility) or when the the mapping $\boldsymbol{\chi}_{\mathbf{x}}^{-1}(\mathbf{x},t)$ is explicitly known, *e.g.* for the description of solids.

1.3.2 Transformation between different Eulerian coordinates

Similar transformations as between the Eulerian and the Lagrangian coordinate system can be performed between two Eulerian descriptions, *e.g.* with respect to $\Omega_{\mathbf{x}}(t)$ and $\Omega_{\mathbf{y}}(t)$.

Consider the two *observers* moving with $\mathbf{v^1}$ and $\mathbf{v^2}$, respectively, and the corresponding velocity fields expressed in Eulerian coordinate system $(\mathbf{x},t) \in \Omega_{\mathbf{x}}(t) \times I$, *i.e.*

$$\Omega_{\mathbf{x}}(t) = \boldsymbol{\chi}_{\mathbf{x}}(\Omega_0,t) \tag{1.212}$$

$$\mathbf{v^1} = \mathbf{v}_{\mathbf{x}}(\mathbf{x},t) = \frac{\partial\, \boldsymbol{\chi}_{\mathbf{x}}}{\partial\, t} \tag{1.213}$$

$$\mathbf{v^2} = \mathbf{v}_{\mathbf{y}}(\mathbf{x},t) \tag{1.214}$$

The velocity $\mathbf{v^2}$, however, also defines an Eulerian coordinate system via

$$\Omega_{\mathbf{y}}(t) = \boldsymbol{\chi}_{\mathbf{y}}(\Omega_0,t) \tag{1.215}$$

$$\mathbf{v^2} = \overline{\mathbf{v}}_{\mathbf{y}}(\mathbf{y},t) = \frac{\partial\, \boldsymbol{\chi}_{\mathbf{y}}}{\partial\, t} \tag{1.216}$$

$$\mathbf{v^1} = \overline{\mathbf{v}}_{\mathbf{x}}(\mathbf{y},t), \tag{1.217}$$

and the transformation between $\Omega_{\mathbf{x}}(t)$ and $\Omega_{\mathbf{y}}(t)$ is desired. Note that the respective velocity fields can also be expressed in Lagrangian coordinates $\boldsymbol{\xi} \in \Omega_0$, *i.e.* $\mathbf{v^1} = \hat{\mathbf{v}}_{\mathbf{x}}(\boldsymbol{\xi},t)$ and $\mathbf{v^2} = \hat{\mathbf{v}}_{\mathbf{y}}(\boldsymbol{\xi},t)$. Consider now the relative motion in $\Omega_{\mathbf{y}}(t)$, *i.e.*

$$\overline{\mathbf{v}}_{\Delta}(\mathbf{y},t) := \overline{\mathbf{v}}_{\mathbf{x}}(\mathbf{y},t) - \overline{\mathbf{v}}_{\mathbf{y}}(\mathbf{y},t) \qquad \mathbf{y} \in \Omega_{\mathbf{y}}(t) \tag{1.218}$$

and the coordinate transformation $T_\eta : \Omega_{\mathbf{y}}(t) \times I \to \Omega_{\mathbf{x}}(t) \times I$ with

$$(\mathbf{y},t) \mapsto T_\eta(\mathbf{y},t) = (\mathbf{y} + \int_{t_0}^{t} \overline{\mathbf{v}}_{\Delta}(\mathbf{y},\tau) d\tau, t) =: (\boldsymbol{\eta}(\mathbf{y},t),t). \tag{1.219}$$

This transformation obeys $\boldsymbol{\eta}(\Omega_{\mathbf{y}}(t)) = \Omega_{\mathbf{x}}(t)$, which is shown in the following auxiliary calculation.

Auxiliary calculation 1.12:

$$\begin{aligned}
\boldsymbol{\eta}(\mathbf{y},t) =& \mathbf{y} + \int_{t_0}^{t} \overline{\mathbf{v}}_{\Delta}(\mathbf{y},\tau)\mathrm{d}\tau \\
=& \mathbf{y} - \int_{t_0}^{t} \overline{\mathbf{v}}_{\mathbf{y}}(\mathbf{y},\tau)\mathrm{d}\tau + \int_{t_0}^{t} \overline{\mathbf{v}}_{\mathbf{x}}(\mathbf{y},\tau)\mathrm{d}\tau \\
\overset{\text{eq.(1.192)}}{=}& \boldsymbol{\chi}_{\mathbf{y}}^{-1}(\mathbf{y},t) + \int_{t_0}^{t} \overline{\mathbf{v}}_{\mathbf{x}}(\mathbf{y},\tau)\mathrm{d}\tau \\
=& \boldsymbol{\xi} + \int_{t_0}^{t} \overline{\mathbf{v}}_{\mathbf{x}}(\mathbf{y},\tau)\mathrm{d}\tau = \boldsymbol{\xi} + \int_{t_0}^{t} \hat{\mathbf{v}}_{\mathbf{x}}(\boldsymbol{\xi},\tau)\mathrm{d}\tau = \boldsymbol{\chi}_{\mathbf{x}}(\boldsymbol{\xi},t) = \mathbf{x}
\end{aligned}$$

The diffeomorphism $\boldsymbol{\eta}(\mathbf{y},t)$ is thus the spatial coordinate transformation obeying

$$\frac{\partial\, \boldsymbol{\eta}(\mathbf{y},t)}{\partial\, t} = \overline{\mathbf{v}}_{\Delta}(\mathbf{y},t). \tag{1.220}$$

Similar to above, an inverse transformation T_{η}^{-1} is declared as

$$T_{\eta}^{-1} : \Omega_{\mathbf{x}}(t) \times I \to \Omega_{\mathbf{y}}(t) \times I \tag{1.221}$$

$$(\mathbf{x},t) \mapsto (\mathbf{x} - \int_{t_0}^{t} \mathbf{v}_{\Delta}(\mathbf{x},\tau)d\tau, t) = (\boldsymbol{\eta}^{-1}(\mathbf{x},t),t). \tag{1.222}$$

The velocity difference $\mathbf{v}^{\mathbf{D}}$ expressed in the respective coordinates is thus

$$\mathbf{v}^{\mathbf{D}} = \hat{\mathbf{v}}_{\Delta}(\boldsymbol{\xi},t) = \mathbf{v}_{\Delta}(\mathbf{x},t) = \overline{\mathbf{v}}_{\Delta}(\mathbf{y},t). \tag{1.223}$$

Using the parametrization $\boldsymbol{\chi}_{\mathbf{x}}$ and $\boldsymbol{\chi}_{\mathbf{y}}$, *i.e.* the diffeomorphism of the respective Eulerian coordinate system to the common Lagrangian description (*c.f.* figure 1.8), and their respective inverses, the motion $\boldsymbol{\eta}$ could be written as a composition

$$\boldsymbol{\eta}(\mathbf{y},t) = \left(\boldsymbol{\chi}_{\mathbf{x}} \circ \boldsymbol{\chi}_{\mathbf{y}}^{-1}\right)(\mathbf{y},t) \tag{1.224}$$

$$\boldsymbol{\eta}^{-1}(\mathbf{x},t) = \left(\boldsymbol{\chi}_{\mathbf{y}} \circ \boldsymbol{\chi}_{\mathbf{x}}^{-1}\right)(\mathbf{x},t). \tag{1.225}$$

Note that $\boldsymbol{\chi}_{\mathbf{y}}^{-1}(\mathbf{y},t) = \boldsymbol{\chi}_{\mathbf{x}}^{-1}(\mathbf{x},t) = \boldsymbol{\xi}$ at time a fixed time t, but $\boldsymbol{\chi}_{\mathbf{y}}^{-1} \not\equiv \boldsymbol{\chi}_{\mathbf{x}}^{-1}$ in general.

Of course the velocity field $\mathbf{v}^{\mathbf{1}}$ and $\mathbf{v}^{\mathbf{2}}$ can be represented in their respective other space coordinates according to the useful relationships

$$\mathbf{v}^{\mathbf{1}} = \mathbf{v}_{\mathbf{x}}(\mathbf{x},t) = \underbrace{\mathbf{v}_{\mathbf{x}}(\boldsymbol{\eta}(\mathbf{y},t),t)}_{=:\overline{\mathbf{v}}_{\mathbf{x}}(\mathbf{y},t)} = \underbrace{\mathbf{v}_{\mathbf{x}}(\boldsymbol{\chi}_{\mathbf{x}}(\boldsymbol{\xi},t),t)}_{=\hat{\mathbf{v}}_{\mathbf{x}}(\boldsymbol{\xi},t)} \tag{1.226}$$

$$\mathbf{v}^{\mathbf{2}} = \overline{\mathbf{v}}_{\mathbf{y}}(\mathbf{y},t) = \underbrace{\overline{\mathbf{v}}_{\mathbf{y}}(\boldsymbol{\eta}^{-1}(\mathbf{x},t),t)}_{=\mathbf{v}_{\mathbf{y}}(\mathbf{x},t)} = \underbrace{\overline{\mathbf{v}}_{\mathbf{y}}(\boldsymbol{\chi}_{\mathbf{y}}(\boldsymbol{\xi},t),t)}_{=\hat{\mathbf{v}}_{\mathbf{y}}(\boldsymbol{\xi},t)}. \tag{1.227}$$

Similar to above the transformation laws for densities and fluxes in the two considered coordinate systems are now derived, finally leading to the transformation law of some balance equation.

Extensive properties in various Eulerian coordinates

Let $A(t)$ be some global (extensive) property[7] with its corresponding density $a(\mathbf{x},t)$ in Eulerian coordinates $\mathbf{x} \in \Omega_{\mathbf{x}}(t)$. The volume integral transformation

$$A(t) = \int\limits_{\Omega_{\mathbf{y}}(t)} a(\boldsymbol{\eta}(\mathbf{y},t),t) \det\left(\mathbf{F}_{\boldsymbol{\eta}}(\mathbf{y},t)\right) \, d\overline{V}(\mathbf{y}) = \int\limits_{\Omega_{\mathbf{y}}(t)} \overline{a}(\mathbf{y},t) \, d\overline{V}(\mathbf{y}), \tag{1.228}$$

with the Eulerian deformation gradient

$$\mathbf{F}_{\boldsymbol{\eta}}(\mathbf{y},t) = \boldsymbol{\nabla}\boldsymbol{\eta}(\mathbf{y},t) \tag{1.229}$$

$$J_{\boldsymbol{\eta}}(\mathbf{y},t) = \det\left(\mathbf{F}_{\boldsymbol{\eta}}(\mathbf{y},t)\right), \tag{1.230}$$

leads to an **alternative Eulerian density**

$$\overline{a}(\mathbf{y},t) := J_{\boldsymbol{\eta}} \cdot a(\boldsymbol{\eta}(\mathbf{y},t),t). \tag{1.231}$$

Fluxes in various Eulerian coordinates

Similar to above, the fluxes are also transformed due to coordinate change from one Eulerian coordinate system to another one.

Let again $\Phi_A(t)$ be the (global) fluxes of some flux Eulerian densities $\mathbf{j}_a(\mathbf{x},t)$. Again from the surface integral transformation one deduces

$$\Phi_A = \int\limits_{\partial\Omega_{\mathbf{x}}(t)} \mathbf{j}_a^{\mathrm{T}} \, d\mathbf{A}(\mathbf{x}) = \int\limits_{\Sigma_{\mathbf{y}}(t)} \det\left(\mathbf{F}_{\boldsymbol{\eta}}\right) \mathbf{j}_a^{\mathrm{T}} \cdot \mathbf{F}_{\boldsymbol{\eta}}^{-\mathrm{T}} \cdot \, d\overline{\mathbf{A}}(\mathbf{y}) \tag{1.232}$$

and thus the respective **alternative Eulerian fluxes**

$$\bar{\mathbf{j}}_a(\mathbf{y},t) := J_{\boldsymbol{\eta}} \cdot \mathbf{F}_{\boldsymbol{\eta}}^{-1}(\mathbf{y},t) \cdot \mathbf{j}_a(\boldsymbol{\eta}(\mathbf{y},t),t). \tag{1.233}$$

Time derivative of extensive properties

The conversion of the local time derivatives is again obtained via Reynolds transport theorem for volume integrals and quite similar to the derivation above. The rate of transient change of a global property $A(t)$ is expressed in the densities $a(\mathbf{x},t),\ \mathbf{x} \in \Omega_{\mathbf{x}}(t)$ and $\overline{a}(\mathbf{y},t),\ \mathbf{y} \in \Omega_{\mathbf{y}}(t)$,

$$\frac{\mathrm{d}\,A(t)}{\mathrm{d}t} = \int\limits_{\Omega_{\mathbf{x}}(t)} \frac{\partial\, a(\mathbf{x},t)}{\partial\, t} + \mathrm{div}_{\mathbf{x}}\left(a(\mathbf{x},t)\mathbf{v}_{\mathbf{x}}(\mathbf{x},t)\right) \, dV(\mathbf{x}) \tag{1.234}$$

$$= \int\limits_{\Omega_{\mathbf{y}}(t)} J_{\eta} \cdot \left(\frac{\partial\, a(\boldsymbol{\eta}(\mathbf{y},t),t)}{\partial\, t} + \mathrm{div}_{\mathbf{x}}\left(a(\mathbf{x},t)\mathbf{v}_{\mathbf{x}}(\mathbf{x},t)\right) \right)\Big|_{\mathbf{x}=\boldsymbol{\eta}(\mathbf{y},t)} d\overline{V}(\mathbf{y}) \tag{1.235}$$

$$= \int\limits_{\Omega_{\mathbf{y}}(t)} \frac{\partial\, \overline{a}(\mathbf{y},t)}{\partial\, t} + \mathrm{div}_{\mathbf{y}}\left(\overline{a}(\mathbf{y},t)\overline{\mathbf{v}}_{\mathbf{y}}(\mathbf{y},t)\right) \, d\overline{V}(\mathbf{y}). \tag{1.236}$$

[7] Of course an equivalent derivation for a vector valued property $\vec{B}$ with the corresponding density $\mathbf{b}(\mathbf{x},t)$ holds

Thus, for $\mathbf{x} = \boldsymbol{\eta}(\mathbf{y}, t)$, one obtains

$$J_{\boldsymbol{\eta}} \cdot \left(\frac{\partial\, a(\mathbf{x}, t)}{\partial\, t} + \mathrm{div}_{\mathbf{x}}\, (a(\mathbf{x}, t)\mathbf{v}_{\mathbf{x}}(\mathbf{x}, t)) \right) = \frac{\partial\, \overline{a}(\mathbf{y}, t)}{\partial\, t} + \mathrm{div}_{\mathbf{y}}\, (\overline{a}(\mathbf{y}, t)\overline{\mathbf{v}}_{\mathbf{y}}(\mathbf{y}, t))\,. \tag{1.237}$$

Transformation of balance equations

With the above definitions and derivations the balance law

$$\frac{\partial\, a(\mathbf{x}, t)}{\partial\, t} = -\mathrm{div}_{\mathbf{x}}\, (a \cdot \mathbf{v}_{\mathbf{x}} + \mathbf{j}_a) + r_a \quad \mathbf{x} \in \Omega_{\mathbf{x}}(t) \tag{1.238}$$

is transformed as

$$\frac{\partial\, \overline{a}(\mathbf{y}, t)}{\partial\, t} = -\mathrm{div}_{\mathbf{y}}\, \left(\overline{a} \cdot \overline{\mathbf{v}}_{\mathbf{y}} + \overline{\mathbf{j}}_a \right) + \overline{r}_a \quad \mathbf{y} \in \Omega_{\mathbf{x}}(t) \tag{1.239}$$

for the variable transformation

$$T_\eta = (\boldsymbol{\eta}(\mathbf{y}, t), t) \tag{1.240}$$

$$\frac{\partial\, \boldsymbol{\eta}(\mathbf{y}, t)}{\partial\, t} = \overline{\mathbf{v}}_\Delta(\mathbf{y}, t), \tag{1.241}$$

with

$$\overline{r}_a(\mathbf{y}, t) := J_{\boldsymbol{\eta}} \cdot r_a(\boldsymbol{\eta}(\mathbf{y}, t), t). \tag{1.242}$$

Summary on coordinate transformations

In theoretical descriptions of physical objects some perspectives are more useful than others, in the sense that the resulting equations are *simpler* or more intuitive. This question arises for example when one considers the flow of a liquid electrolyte. Since the liquid itself moves, one could *sit in the liquid* and describe the physics around it relative to the motion of the liquid. On the other hand, the electrolyte may carry an electric current, which does not necessarily coincide with the flow of mass. It is thus also interesting to describe the field equations of the liquid with respect to the electric current. The description of $\mathbf{x}$ and $\mathbf{y}$ is just arbitrary, however useful to distinguish between different perspectives. The coordinate transformation are then used to transform the final balance equations (*i.e.* of mass, momentum, entropy) to a desired or appropriate frame of reference.

2

Coupled Thermo- and Electrodynamics

In this chapter a field theory of coupled thermo- and electrodynamics is developed. Based on classical physical principles, such as conservation of

- mass,
- momentum,
- and energy,

respective balance equations are be derived. With the introduction of an entropy function, relating the independent physical properties, thermodynamics arises in the framework. In that sense a local version of the second law of thermodynamics is introduced, stating that the entropy production is strictly non-negative. This leads to some conditions on the material and heat flux as well as on polarization and magnetization. A set of PDEs (a model) is said to be *thermodynamic consistent* if it fulfills this condition.
Variable exchange and transformations are further described, allowing for an exchange of dependent properties (*e.g.* internal energy and temperature) which lead to the Helmholtz free energy and the Gibbs free energy.
After the derivation of this general framework, some explicit material functions are stated, modeling for example an incompressible liquid electrolyte or a solid with some mobile, charged species.

2.1 Introduction

A field theoretical formulation of thermo- and electrodynamics requires a continuum hypothesis. Even though the term is frequently used, various definitions or alternative appellations are found in literature. Ross[8], for example, mentions in his work "On the Problem of Defining Local Thermodynamic Equilibrium"

> There are two statements which may come to your mind when reading the title of this paper: "Everybody knows what local thermodynamic equilibrium means", and: "Nobody has ever given a a really satisfactory definition of local thermodynamic equilibrium (LTE)".

A possible definition given by him is: "A system is in local thermodynamic equilibrium at a given time if there is a well-defined temperature $T(\mathbf{x})$ at any macroscopic point $\mathbf{x}$" [8]. This coincides with sustaining local Maxwell–Boltzmann-distributions due to small and slow changes of thermodynamic properties. However, LTE could also serve as the very basis to *allow* for a local formulation of thermodynamics in terms of continuous space and time dependent properties. Nevertheless I will not use the term *local thermodynamic equilibrium*, however, in some sense it corresponds to my definition of continuum hypothesis.

Definition 7 (Continuum hypothesis)**.**

Consider a scalar physical (extensive) property $A(t)$ with its corresponding densities $a(\mathbf{x},t)$ in $\Omega(t)$ and $\underset{\mathrm{s}}{a}(\mathbf{x},t)$ on the surface Σ, satisfying the global balance equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\int\limits_{\Omega} a(\mathbf{x},t)\,dV + \int\limits_{\Sigma} \underset{\mathrm{s}}{a}(\mathbf{x},t)\,dA(\mathbf{x})\right) = -\int\limits_{\partial\Omega} \mathbf{j}_a(\mathbf{x},t)^{\mathrm{T}}\cdot d\mathbf{A}(\mathbf{x}) - \int\limits_{\partial\Sigma} \underset{\mathrm{s}}{\mathbf{j}}_a(\mathbf{x},t)^{\mathrm{T}}\cdot d\mathbf{s}(\mathbf{x}) + \int\limits_{\Omega} r_a(\mathbf{x},t)\,dV(\mathbf{x}) + \int\limits_{\Sigma} \underset{\mathrm{s}}{r}_a(\mathbf{x},t)\,dA(\mathbf{x}). \tag{2.1}$$

In the proceeding chapter it has been shown that the local equations of balance

$$\frac{\partial\, a(\mathbf{x},t)}{\partial\, t} = -\mathrm{div}\left(a(\mathbf{x},t)\cdot\mathbf{v}(\mathbf{x},t) + \mathbf{j}_a(\mathbf{x},t)\right) + r_a(\mathbf{x},t) \qquad \forall\mathbf{x}\in\Omega \tag{2.2}$$

$$\frac{\partial\, \underset{\mathrm{s}}{a}}{\partial\, t} = -\underset{\mathrm{s}}{\mathrm{div}}\left(\underset{\mathrm{s}}{a}\,\underset{\mathrm{s}}{\mathbf{v}} + \underset{\mathrm{s}}{\mathbf{j}}_a\right) - \kappa\,\underset{\mathrm{s}}{a}v_n + \underset{\mathrm{s}}{r}_a - [\![a\mathbf{v}^{\mathrm{T}} + \mathbf{j}_a^{\mathrm{T}}]\!]\cdot\mathbf{n} \qquad \forall\mathbf{x}\in\Sigma. \tag{2.3}$$

are obtained if the global equations hold **for every** $\omega\in\Omega$ and $\sigma\in\Sigma$. This is raised to the **definition of the continuum hypothesis**, stating the local balance equations are valid throughout the whole domain of interest.

Of course, many situations in physics and chemistry arise where this definition may fail, *e.g.* the description of a large molecule in terms of atom densities. On the atomic scale the explicit representation of each atom and some interaction potential between these atoms is much more appropriate. Nevertheless, the density formulation of particles (in particular electrons) is (again) a very precise method of approximation[9] on the atomic scale. However, the explicit *material functions* to describe a specific molecule or ensemble are far more complex and often unknown.

2.1.1 Conservation of mass and charge

Within a domain Ω, which covers some singular surface $\Sigma\subset\Omega$, mass M_α of $\alpha = 1,\ldots,\mathrm{n}$ species may somehow be distributed in space.

Assumption 1 (Continuous mass density)**.**

It is assumed that the distribution of an overall mass M_α may be (uniquely) written as

$$M_\alpha = \int\limits_{\Omega} \rho_\alpha\,dV + \int\limits_{\Sigma} \underset{\mathrm{s}}{\rho}_\alpha\,dA \tag{2.4}$$

with mass densities ρ_α in Ω and $\underset{\mathrm{s}}{\rho}_\alpha$ in Σ.[1] Further, M_α is assumed to fulfill the continuum hypothesis.

Note that not each species is necessarily present in Ω and Σ, *e.g.* intermediates in surface reactions or uncharged, adsorbed species, which simply entails $\rho_\alpha \equiv 0$ or $\underset{\mathrm{s}}{\rho}_\alpha \equiv 0$, respectively. However, the index set $\mathrm{N} = \{1, \ldots, \mathrm{n}\}$ covers **all** species which are present in the physical object. With the specific mass m_α per atom of the species α one obtains the respective number densities

$$n_\alpha = \frac{\rho_\alpha}{m_\alpha} \qquad \alpha = 1, \ldots, \mathrm{n} \tag{2.5}$$

$$\underset{\mathrm{s}}{n}_\alpha = \frac{\underset{\mathrm{s}}{\rho}_\alpha}{m_\alpha} \qquad \alpha = 1, \ldots, \mathrm{n}, \tag{2.6}$$

and straight forward the total amount N_α of a species. The mass fraction w_α is

$$w_\alpha = \frac{\rho_\alpha}{\rho} \qquad \alpha = 1, \ldots, \mathrm{n} \tag{2.7}$$

and the mole fraction c_α (sometimes also called concentration)

$$c_\alpha = \frac{n_\alpha}{n} \qquad \alpha = 1, \ldots, \mathrm{n}. \tag{2.8}$$

Each species may carry a charge $e_0 z_\alpha$ with which the charge densities

$$n_\alpha^{\mathrm{F}} = e_0 z_\alpha n_\alpha = \frac{e_0 z_\alpha}{m_\alpha} \rho_\alpha \qquad \alpha = 1, \ldots, \mathrm{n} \tag{2.9}$$

$$\underset{\mathrm{s}}{n}_\alpha^{\mathrm{F}} = e_0 z_\alpha \underset{\mathrm{s}}{n}_\alpha = \frac{e_0 z_\alpha}{m_\alpha} \underset{\mathrm{s}}{\rho}_\alpha \qquad \alpha = 1, \ldots, \mathrm{n} \tag{2.10}$$

arise. The superscript ^{F} already denotes *free charge*, in contrast to polarization charge, which is introduced later in this chapter. The overall mass, charge and species densities are then simply

$$\rho = \sum_{\alpha=1}^{\mathrm{n}} \rho_\alpha, \quad n^{\mathrm{F}} = \sum_{\alpha=1}^{\mathrm{n}} n_\alpha^{\mathrm{F}} \quad \text{and} \quad n = \sum_{\alpha=1}^{\mathrm{n}} n_\alpha.$$

2.1.2 Balance equation

While in chapter (1.2) the structure of global and local balance equation were investigated, their *origin* was not rigorously stated. This circumstance meets the following assumption.

Assumption 2 (Balance equation representation)**.**

It is **assumed** that the mass density of each species may vary in time **only** due to

- a volume flux J_α with mass flux density $\mathbf{j}_\alpha(\mathbf{x}, t)$ $\left[\frac{\mathrm{kg}}{\mathrm{sm}^2}\right]$ and

$$J_\alpha = -\oint_{\partial\Omega} \mathbf{j}_\alpha^{\mathrm{T}} \cdot d\mathbf{A},$$

[1] If the boundary of Ω additionally carries some surface mass density $\underset{\mathrm{s}}{\rho}$ the definition is just extended an analogy.

- a volumetric production rate R_α with mass production $r_\alpha(\mathbf{x},t)$ $\left[\frac{\mathrm{kg}}{\mathrm{sm}^3}\right]$

$$R_\alpha = \int_\Omega r_\alpha \, dV,$$

- a Surface flux $\underset{\mathrm{s}}{J}_\alpha$ with a tangential flux density $\underset{\mathrm{s}}{\mathbf{j}}_\alpha(\mathbf{x},t)$ $\left[\frac{\mathrm{kg}}{\mathrm{sm}}\right]$ and

$$\underset{\mathrm{s}}{J}_\alpha = -\oint_{\partial\Sigma} \underset{\mathrm{s}}{\mathbf{j}}_\alpha^{\mathrm{T}} \cdot d\mathbf{A},$$

- and a surface production $\underset{\mathrm{s}}{R}_\alpha$ with local rate $\underset{\mathrm{s}}{r}_\alpha(\mathbf{x},t)$ $\left[\frac{\mathrm{kg}}{\mathrm{sm}^2}\right]$ and

$$\underset{\mathrm{s}}{R}_\alpha = \int_\Sigma \underset{\mathrm{s}}{r}_\alpha \, dV.$$

Further, a continuum hypothesis for the flux and source densities is **assumed**, leading to the local balance equations

$$\frac{\partial \rho_\alpha(\mathbf{x},t)}{\partial t} = -\mathrm{div}\left(\rho_\alpha(\mathbf{x},t)\cdot\mathbf{v}(\mathbf{x},t) + \mathbf{j}_\alpha(\mathbf{x},t)\right) + r_\alpha(\mathbf{x},t) \qquad \forall \mathbf{x}\in\Omega \tag{2.11}$$

$$\frac{\partial \underset{\mathrm{s}}{\rho}_\alpha(\mathbf{x},t)}{\partial t} = -\underset{\mathrm{s}}{\mathrm{div}}\left(\underset{\mathrm{s}}{\rho}_\alpha \underset{\mathrm{s}}{\mathbf{v}} + \underset{\mathrm{s}}{\mathbf{j}}_\alpha\right) - \kappa \underset{\mathrm{s}}{\rho}_\alpha v_n + \underset{\mathrm{s}}{r}_\alpha - [\![\rho_\alpha \mathbf{v}^{\mathrm{T}} + \mathbf{j}_\alpha^{\mathrm{T}}]\!]\cdot\mathbf{n} \qquad \forall \mathbf{x}\in\Sigma. \tag{2.12}$$

Here, $\mathbf{v}(\mathbf{x},t)$ $\left[\frac{\mathrm{m}}{\mathrm{s}}\right]$ is some *arbitrary*[2] Eulerian velocity field, with normal component v_n and tangential component $\underset{\mathrm{s}}{\mathbf{v}}$. The curvature of the material surface [3] Σ is denoted by κ.

The conservation of the overall mass density

$$\rho = \sum_{\alpha=1}^{\mathrm{n}} \rho_\alpha, \tag{2.13}$$

which is deduced rigorously in the next subsection, requires

$$\frac{\partial \rho}{\partial t} = -\mathrm{div}\,(\rho\mathbf{v} + \mathbf{j}) \tag{2.14}$$

$$\overset{!}{=} -\mathrm{div}\left(\rho\mathbf{v} + \sum_{\alpha=1}^{\mathrm{n}} \mathbf{j}_\alpha\right), \tag{2.15}$$

where $\mathbf{j}$ is the **(diffusive) mass flux** and

$$\mathbf{i} := \rho\mathbf{v} + \mathbf{j} \tag{2.16}$$

[2]The actual physical balance equation is of course independent of the coordinate system. However, an appropriate **choice** of coordinate system simplifies the formulation of some physical properties, *e.g.* Newtons second law. Such an explicit choice is stated in remark 4 as standard coordinate system.

[3]Even though the velocity field $\mathbf{v}$ is yet undetermined, only singular surfaces which move with $\mathbf{v}$ (material surfaces) are considered.

the total mass flux . Yet, this restriction should be read as

$$\sum_{\alpha=1}^{\mathrm{n}} \mathbf{j}_\alpha \stackrel{!}{=} \mathbf{j}, \tag{2.17}$$

which states that (diffusive) mass flux is not independent and called **mass flux constraint**. Similar, the conservation of free charge

$$n^{\mathrm{F}} = e_0 \sum_{\alpha=1}^{\mathrm{n}} \frac{z_\alpha}{m_\alpha} \rho_\alpha \tag{2.18}$$

requires

$$\frac{\partial n^{\mathrm{F}}}{\partial t} = -\operatorname{div}\left(n^{\mathrm{F}}\mathbf{v} + \mathbf{j}^{\mathrm{F}}\right) \tag{2.19}$$

$$\stackrel{!}{=} -\operatorname{div}\left(n^{\mathrm{F}}\mathbf{v} + e_0 \sum_{\alpha=1}^{\mathrm{n}} \frac{z_\alpha}{m_\alpha} \mathbf{j}_\alpha\right) \tag{2.20}$$

and thus

$$e_0 \sum_{\alpha=1}^{\mathrm{n}} \frac{z_\alpha}{m_\alpha} \mathbf{j}_\alpha \stackrel{!}{=} \mathbf{j}^{\mathrm{F}}. \tag{2.21}$$

Accordingly, the flux $\mathbf{j}^{\mathrm{F}}$ is called **diffusional (free charge) electric current** and

$$\mathbf{i}^{\mathrm{F}} := n^{\mathrm{F}}\mathbf{v} + \mathbf{j}^{\mathrm{F}} \tag{2.22}$$

is called **total (free charge) current**.

Remark 3 (Flux constraint).

For a mixture, consisting of n species, the conservation of mass implies

$$\rho = \sum_{\alpha=1}^{\mathrm{n}} \rho_\alpha \qquad \forall(\mathbf{x}, t) \in \Omega \times I \tag{2.23}$$

$$\text{and} \qquad \mathbf{j} = \sum_{\alpha=1}^{\mathrm{n}} \mathbf{j}_\alpha \qquad \forall(\mathbf{x}, t) \in \Omega \times I, \tag{2.24}$$

independent of the frame of reference (*c.f.* the concept of observer velocities in section 1.3.2). An explicit choice of coordinate system fixes in addition one of the remaining fluxes $(\mathbf{j}_1, \ldots, \mathbf{j}_n)$, resulting in $\mathrm{n} - 1$ independent material fluxes.

Yet, the set of balance equations are rather general, in the sense that the actual Eulerian coordinate system $(\mathbf{x}, \mathbf{v})$, $\mathbf{x} \in \Omega$ is still arbitrary. Of course, various useful frames of reference exist, and one is free to choose an appropriate (inertial) frame of reference. An **exclusive frame of reference** $(\mathbf{x}, \mathbf{v})$ is, however, the one which is **chosen** such that

$$\mathbf{j}(\mathbf{x}, t) = \mathbf{0} \qquad \forall(\mathbf{x}, t) \in \Omega \times I, \tag{2.25}$$

and thus

$$\frac{\partial \rho(\mathbf{x},t)}{\partial t} = -\mathrm{div}\,(\rho(\mathbf{x},t)\,\mathbf{v}(\mathbf{x},t)) \tag{2.26}$$

$$\sum_{\alpha=1}^{\mathrm{n}} \mathbf{j}_\alpha(\mathbf{x},t) = \mathbf{0}. \tag{2.27}$$

In this case, the velocity field $\mathbf{v}(\mathbf{x},t)$ is called **barycentric velocity** and the coordinate system $(\mathbf{x},\mathbf{v}),\ \mathbf{x}\in\Omega$ with

$$(\mathbf{x},t) = (\boldsymbol{\chi}(\boldsymbol{\xi},t),t) \qquad \mathbf{x}\in\Omega,\ \boldsymbol{\xi}\in\Omega_0 \tag{2.28}$$

$$\frac{\partial \boldsymbol{\chi}_{\mathbf{x}}(\boldsymbol{\xi},t)}{\partial t} = \hat{\mathbf{v}}(\boldsymbol{\xi},t) = \mathbf{v}(\mathbf{x},t) \tag{2.29}$$

is classically called **material description** of the mixture (or standard Eulerian coordinate system). Many authors [5, 10, 11] *begin* their derivation already with the unique coordinate system, satisfying $\mathbf{j}=0$. This somehow *hides* the existence of $\mathbf{j}$, which in another coordinate system does not necessarily vanish. Consider for example a frame of reference $(\boldsymbol{\xi},\hat{\mathbf{v}}),\ \boldsymbol{\xi}\in\Omega$ which is chosen such that

$$\hat{\mathbf{j}}_{\mathrm{n}}(\boldsymbol{\xi},t) = 0 \tag{2.30}$$

and

$$\frac{\partial \rho_{\mathrm{n}}(\boldsymbol{\xi},t)}{\partial t} = -\mathrm{div}_{\boldsymbol{\xi}}\,(\rho_{\mathrm{n}}(\boldsymbol{\xi},t)\,\hat{\mathbf{v}}(\boldsymbol{\xi},t)). \tag{2.31}$$

In this case, the mass flux constraint eq. (2.17) implies

$$\sum_{\alpha=1}^{\mathrm{n}-1} \hat{\mathbf{j}}_\alpha(\boldsymbol{\xi},t) = \hat{\mathbf{j}}(\boldsymbol{\xi},t) \neq \mathbf{0}. \tag{2.32}$$

A more precise discussion on coordinate (or flux) transformations is given in section 1.3.

Remark 4 (Standard coordinate system).

The standard coordinate system, if not explicitly noted otherwise, will be $(\mathbf{x},\mathbf{v}),\ \mathbf{x}\in\Omega$ such that

$$\mathbf{j}(\mathbf{x},t) = \mathbf{0} \tag{2.33}$$

$$\frac{\partial \rho(\mathbf{x},t)}{\partial t} = -\mathrm{div}\ (\rho\mathbf{v}(\mathbf{x},t)) \tag{2.34}$$

with the barycentric velocity $\mathbf{v}$.

2.1.3 Chemical reactions

Let X_α denote the actual chemical molecule, *e.g.* Li^+, PF_6^- or DMC (Dimethylcarbonate $OC(OCH_3)_2$). The system might be subject to n_r chemical reactions of the type

$$\nu'_{1,k}X_1 + \cdots + \nu'_{n,k}X_n \rightleftharpoons \nu''_{1,k}X_1 + \cdots + \nu''_{n,k}X_n \qquad k = 1, \ldots, n_r \tag{2.35}$$

with $\nu_{\alpha,k} := \nu''_{\alpha,k} - \nu'_{\alpha,k}$ being the net stochiometric coefficient .

Assumption 3 (Detailed balance)**.**

It is assumed that the mass production (or annihilation) for each species is

$$r_\alpha(\mathbf{x}, t) = \sum_{k=1}^{n_r} \nu_{\alpha,k}\, m_\alpha \cdot q_k(\mathbf{x}, t) \tag{2.36}$$

and q_k the production (or annihilation) rate of particles in each reaction. I will call equation (2.36) **detailed balance** [12].

An explicit function q_k (reaction model) will be derived in section 2.7 and extended in section 3.5 to derive the mass action law.

Assumption 4 (Conservation of mass and charge in chemical reactions)**.**

It will be assumed that in each reaction (thus also on surface reactions) $k \in \{1, \ldots, n_r\}$ mass and charge is conserved, *i.e.*

$$\sum_{\alpha=1}^{n} \nu_{\alpha,k} \cdot m_\alpha = 0, \qquad k = 1, \ldots, n_r \tag{2.37}$$

$$\sum_{k=1}^{n} \nu_{\alpha,k} \cdot z_k = 0, \qquad k = 1, \ldots, n_r. \tag{2.38}$$

This coefficient constraints imply the conservation of mass and charge densities.

Corollary 5 (Conservation of mass and charge)**.**

Summing all mass balance equations (2.11), the balance equation of ρ (in the standard coordinate system) is

$$\frac{\partial \rho}{\partial t} = -\mathrm{div}\ (\rho \mathbf{v}) + \sum_{\alpha=1}^{n} r_\alpha. \tag{2.39}$$

Since

$$\sum_{\alpha=1}^{n} r_\alpha = \sum_{\alpha=1}^{n} \sum_{k=1}^{n_r} \nu_{\alpha,k} \cdot m_\alpha q_k = \sum_{k=1}^{n_r} q_k \sum_{\alpha=1}^{n} \nu_{\alpha,k} \cdot m_\alpha = 0, \tag{2.40}$$

the *source of mass* vanishes and **mass is conserved**. Similar, the balance of free charge is

$$\frac{\partial n^F}{\partial t} = -\mathrm{div}\left(n^F \mathbf{v} + \sum_{\alpha=1}^{n} \frac{e_0 z_\alpha}{m_\alpha} \mathbf{j}_\alpha\right) + \sum_{\alpha=1}^{n} \frac{e_0 z_\alpha}{m_\alpha} r_\alpha \tag{2.41}$$

and the *source of charge* vanishes due to

$$\sum_{\alpha=1}^{\mathrm{n}} \frac{e_0 z_\alpha}{m_\alpha} r_\alpha = e_0 \sum_{k=1}^{\mathrm{n}_r} q_k \sum_{\alpha=1}^{\mathrm{n}} \nu_{\alpha,k} \cdot z_\alpha = 0. \tag{2.42}$$

Hence, the balance equation of charge is a conservation equation and the **free charge is conserved**.

On the singular surface Σ, let Y_α denote surface (or adsorbed) molecules, *e.g.* $\mathrm{Li}_{(\mathrm{ad})}$, $\mathrm{OH}-_{(\mathrm{ad})}$ or $\mathrm{e}^-_{(\mathrm{ad})}$ (an electron at the surface of an electrode), which undergo surface reactions

$$\underset{\mathrm{s}}{\nu}'_{1,k} \mathrm{Y}_1 + \cdots + \underset{\mathrm{s}}{\nu}'_{\mathrm{n},k} \mathrm{Y}_\mathrm{n} \underset{\mathrm{b}}{\overset{\mathrm{f}}{\rightleftharpoons}} \underset{\mathrm{s}}{\nu}''_{1,k} \mathrm{Y}_1 + \cdots + \underset{\mathrm{s}}{\nu}''_{\mathrm{n},k} \mathrm{Y}_\mathrm{n} \qquad k = 1, \ldots, \underset{\mathrm{s}}{\mathrm{n}}_r. \tag{2.43}$$

Like above, a detailed balance condition is assumed for surface reactions, leading to the mass production rate

$$\underset{\mathrm{s}}{r}_\alpha = \sum_{\alpha=1}^{\mathrm{n}} \underset{\mathrm{s}}{\nu}_{\alpha,k}\, m_\alpha \cdot \underset{\mathrm{s}}{q}_k \qquad \alpha = 1, \ldots, \mathrm{n} \tag{2.44}$$

with the net surface stochiometric coefficient

$$\underset{\mathrm{s}}{\nu}_{\alpha,k} := \underset{\mathrm{s}}{\nu}''_{\alpha,k} - \underset{\mathrm{s}}{\nu}'_{\alpha,k} \tag{2.45}$$

and the reaction rate $\underset{\mathrm{s}}{q}_k, k = 1, \ldots \underset{\mathrm{s}}{\mathrm{n}}_r$. Clearly, charge and mass is also conserved in surface reactions, which imply the constraints

$$\sum_{\alpha=1}^{\mathrm{n}} \underset{\mathrm{s}}{\nu}_{\alpha,k} \cdot m_\alpha = 0, \qquad k = 1, \ldots, \underset{\mathrm{s}}{\mathrm{n}}_r \tag{2.46}$$

$$\sum_{k=1}^{n} \underset{\mathrm{s}}{\nu}_{\alpha,k} \cdot z_k = 0, \qquad k = 1, \ldots, \underset{\mathrm{s}}{\mathrm{n}}_r. \tag{2.47}$$

Again, similar to volumetric conservation of mass and free charge density, these constraints lead to conservation of surface mass and charge density.

2.2 Electrodynamics of continuous media

Of course the modern form of Maxwells equations are well know in theoretical physics and mathematics for more than a century. However, in the context of electrochemistry a consistent usage of a thermo-electrodynamic framework is yet at its very beginning. A realistic and thermodynamic consistent description of a metal/electrolyte interface, for example, requires more knowledge than a stoic application of the Poisson–Boltzmann-equation. Many electrochemical phenomena are still not (well) understood[13], and classical *a priori* assumptions made in the past are doubtable. For an in-depth understanding of the complex interplay between (surface) chemistry and electrodynamics a *consistent* derivation of the field equations is very illustrative.

2.2.1 Derivation of Maxwells equations

An interesting derivation of the set of Maxwell equations in terms of balance equations was considered by I. Müller [5]. Consider the global balance equations of a **conserved** scalar property A with its respective and densities and fluxes, *i.e.*

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\int_{\Omega} a(\mathbf{x},t)\,dV + \int_{\Sigma} \underset{\mathrm{s}}{a}(\mathbf{x},t)\,dA\right) = -\oint_{\partial\Omega} \mathbf{j}_a^{\mathrm{T}}(\mathbf{x},t)\cdot d\mathbf{A} - \oint_{\partial\Sigma} \underset{\mathrm{s}}{\mathbf{j}_a^{\mathrm{T}}}\cdot d\mathbf{s} \tag{2.48}$$

Now, consider the following **Ansatz**, where the vector fields $\mathbf{b}$ and $\mathbf{c}$ are chosen such that

$$\oint_{\partial\Omega} \mathbf{b}^{\mathrm{T}}(\mathbf{x},t)\cdot d\mathbf{A} = \int_{\Omega} a(\mathbf{x},t)\,dV + \int_{\Sigma} \underset{\mathrm{s}}{a}(\mathbf{x},t)\,dA \tag{2.49}$$

$$\oint_{\partial\Omega} \mathbf{c}^{\mathrm{T}}(\mathbf{x},t)\cdot d\mathbf{A} = 0. \tag{2.50}$$

Their corresponding balance equations are

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\sigma} \mathbf{b}^{\mathrm{T}}\cdot d\mathbf{A} = -\oint_{\partial\sigma} \mathbf{j}_{\mathbf{b}}^{\mathrm{T}}\cdot d\mathbf{s} + \int_{\sigma} \mathbf{r}_{\mathbf{b}}^{\mathrm{T}}\cdot d\mathbf{A} + \int_{\psi} \underset{\mathrm{s}}{\mathbf{r}_{\mathbf{b}}^{\mathrm{T}}}\cdot d\mathbf{s} \tag{2.51}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\sigma} \mathbf{c}^{\mathrm{T}}\cdot d\mathbf{A} = -\oint_{\partial\sigma} \mathbf{j}_{\mathbf{c}}^{\mathrm{T}}\cdot \mathbf{s} \tag{2.52}$$

for any $\sigma \in \Omega$ and $\psi = \sigma \cap \Sigma$. The fluxes $\mathbf{j}_{\mathbf{b}}$ and $\mathbf{j}_{\mathbf{c}}$ are chosen as

$$\mathbf{b} = -\varepsilon_0\left(\mathbf{j}_{\mathbf{c}} + \mathbf{c}\times\mathbf{v}\right) \tag{2.53}$$

$$\mathbf{c} = \mu_0\left(\mathbf{j}_{\mathbf{b}} + \mathbf{b}\times\mathbf{v}\right) \tag{2.54}$$

with some constants ε_0 and μ_0, which couples the set of equations. Hence the equation system is coupled and one obtains the (formal) **solution** of eq. (2.48) as

$$-\oint_{\partial\Omega} \mathbf{j}_a^{\mathrm{T}}(\mathbf{x},t)\cdot d\mathbf{A} - \oint_{\partial\Sigma} \underset{\mathrm{s}}{\mathbf{j}_a^{\mathrm{T}}}\cdot d\mathbf{s} = \int_{\partial\Omega} \mathbf{r}_{\mathbf{b}}^{\mathrm{T}}\cdot d\mathbf{A} + \int_{\partial\Sigma} \underset{\mathrm{s}}{\mathbf{r}_{\mathbf{b}}^{\mathrm{T}}}\cdot d\mathbf{s} \tag{2.55}$$

if $\sigma \to \partial\Omega$ and thus $\psi \to \partial\Sigma$. Hence the currents $\mathbf{j}_a$ and $\underset{\mathrm{s}}{\mathbf{j}_a}$ correspond to the source terms of $\mathbf{b}$, *i.e.*

$$\mathbf{r}_{\mathbf{b}} = -\mathbf{j}_a \tag{2.56}$$

$$\underset{\mathrm{s}}{\mathbf{r}_{\mathbf{b}}} = -\underset{\mathrm{s}}{\mathbf{j}_a} \tag{2.57}$$

and the source terms of $\mathbf{c}$ vanish, *i.e.*

$$\mathbf{r}_{\mathbf{c}} = \mathbf{0} \tag{2.58}$$

$$\underset{\mathrm{s}}{\mathbf{r}_{\mathbf{c}}} = \mathbf{0}. \tag{2.59}$$

Next, equations (2.49) and (2.50) are again assumed to hold for every $\omega \in \Omega$ (continuum

hypothesis), leading to

$$\nabla \cdot \mathbf{b} = a \quad \mathbf{x} \in \Omega \qquad\qquad [\![\mathbf{b}^{\mathrm{T}}]\!] \cdot \mathbf{n} = \underset{\mathrm{s}}{a} \quad \mathbf{x} \in \Sigma \tag{2.60}$$

$$\nabla \cdot \mathbf{c} = 0 \quad \mathbf{x} \in \Omega \qquad\qquad [\![\mathbf{c}^{\mathrm{T}}]\!] \cdot \mathbf{n} = 0 \quad \mathbf{x} \in \Sigma. \tag{2.61}$$

Comparing eq. (2.51) and (2.52) to the local flux balance equations (*c.f.* section 1.2.3)

$$\frac{\partial\, \mathbf{b}(\mathbf{x},t)}{\partial\, t} = -\mathrm{curl}\left((\mathbf{j_b}(\mathbf{x},t) + \mathbf{b}(\mathbf{x},t) \times \mathbf{v}(\mathbf{x},t)\right) - (\mathrm{div}\, \mathbf{b}) \cdot \mathbf{v}(\mathbf{x},t) + \mathbf{r_b}(\mathbf{x},t) \tag{2.62}$$

$$\underset{\mathrm{s}}{\mathbf{r_b}}(\mathbf{x},t) = [\![\mathbf{j_b}(\mathbf{x},t) + \mathbf{b}(\mathbf{x},t) \times \mathbf{v}(\mathbf{x},t)]\!] \tag{2.63}$$

(and similar for $\mathbf{c}$) finally leads to

$$\frac{\partial\, \mathbf{b}}{\partial\, t} = -\mathrm{curl}\left(\mathbf{j_b} + \mathbf{b} \times \mathbf{v}\right) - a \cdot \mathbf{v} - \mathbf{j}_a = \frac{1}{\mu_0}\mathrm{curl}\left(\mathbf{c}\right) - a \cdot \mathbf{v} - \mathbf{j}_a \tag{2.64}$$

$$-\underset{\mathrm{s}}{\mathbf{j}_a} = [\![\mathbf{j_b} + \mathbf{b} \times \mathbf{v}]\!] = -\frac{1}{\mu_0}[\![\mathbf{c}]\!] \tag{2.65}$$

and

$$\frac{\partial\, \mathbf{c}}{\partial\, t} = -\mathrm{curl}\left(\mathbf{j_c} + \mathbf{c} \times \mathbf{v}\right) = -\frac{1}{\varepsilon_0}\mathrm{curl}\left(\mathbf{b}\right) \tag{2.66}$$

$$\mathbf{0} = [\![\mathbf{j_c} + \mathbf{c} \times \mathbf{v}]\!] = [\![\mathbf{b}]\!]. \tag{2.67}$$

Note that the results are obtained from surface integral balance equations by considering a surface element σ which is completely in Ω and intersects the singular surface Σ with the line element ψ. A variation of *all* $\sigma \in \Omega$ finally leads to the local flux balance equations. The jump conditions through a singular line, which were derived in 1.2.3 (*c.f.* eq. (1.183) and fig. 1.7), denote the jump in binormal direction $\mathbf{b}$ of σ. However, with the construction of σ and $\psi = \sigma \cap \Sigma$, the binormal $\mathbf{b}$ of ψ is actually the normal of Σ and the jump brackets in eqs. (2.85) and (2.85) really denote the flux jump in normal direction across Σ.

2.2.2 Electromagnetic field and flux densities

Assumption 5 (Electric and magnetic flux densities)**.**

It is assumed that the electromagnetic field is described with the

- Electric flux density $\mathbf{D}$ $\left[\frac{\mathrm{C}}{\mathrm{m}^2}\right]$,
- Magnetic flux density $\mathbf{B}$ $[\,\mathrm{T}\,]$,
- Electric field $\mathbf{E}$ $\left[\frac{\mathrm{V}}{\mathrm{m}}\right]$,
- and Magnetic field[4] $\mathbf{H}$ $\left[\frac{\mathrm{A}}{\mathrm{m}}\right]$,

[4] I will follow the notation given by I. Müller [5] in contrast to *classical* syntax conventions of electrodynamics, where $\mathbf{D}$ is usually denotes the displacement field. However, I will avoid at all the definition of the displacement field. Nevertheless, a distinction between the electric flux density $\mathbf{D}$ and $\mathbf{E}$ is very illustrative.

and that these vector fields fulfill the balance equations (2.64) - (2.67) with the choice

$$a = n^{\mathrm{F}} \qquad \underset{\mathrm{s}}{a} = \underset{\mathrm{s}}{n}^{\mathrm{F}} \tag{2.68}$$

$$\mathbf{j}_a = \mathbf{j}^{\mathrm{F}} \qquad \underset{\mathrm{s}}{\mathbf{j}_a} = \underset{\mathrm{s}}{\mathbf{j}}^{\mathrm{F}} \tag{2.69}$$

$$\mathbf{b} = \mathbf{D} \qquad \mathbf{c} = \mathbf{B} \tag{2.70}$$

$$\mathbf{j_b} = \mathbf{H} \qquad \mathbf{j_c} = -\,\mathbf{E}. \tag{2.71}$$

The coupling (2.53) claims

$$\mathbf{b} = -\varepsilon_0 \cdot (\mathbf{j_c} + \mathbf{c} \times \mathbf{v}) \tag{2.72}$$

$$\mathbf{c} = \mu_0 \cdot (\mathbf{j_b} + \mathbf{b} \times \mathbf{v}) \tag{2.73}$$

which are the general Maxwell–Lorentz relations

$$\mathbf{D} = \varepsilon_0(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \tag{2.74}$$

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{D} \times \mathbf{v}) \tag{2.75}$$

in an **arbitrary frame of reference**. It is more common to write the last equation as

$$\mathbf{H} = \frac{1}{\mu_0}\mathbf{B} - \mathbf{D} \times \mathbf{v} = \frac{1}{\mu_0}\mathbf{B} - \varepsilon_0(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \times \mathbf{v} \tag{2.76}$$

$$= \frac{1}{\mu_0}\mathbf{B} - \varepsilon_0\mathbf{E} \times \mathbf{v} + \frac{1}{c_0^0}\mathbf{v} \times (\mathbf{v} \times \frac{1}{\mu_0}\mathbf{B}). \tag{2.77}$$

With the Graßmann identity (A.28) this could be rewritten as

$$\mathbf{H} = \frac{1}{\mu_0}\mathbf{B} - \varepsilon_0\mathbf{E} \times \mathbf{v} + \frac{1}{c_0^0}\left(\mathbf{v} \otimes \mathbf{v} - \langle \mathbf{v}, \mathbf{v} \rangle \cdot \mathbf{Id}\right) \cdot \frac{1}{\mu_0}\mathbf{B} \tag{2.78}$$

$$= \frac{1}{\mu_0}\left(\left(1 - \frac{\langle \mathbf{v}, \mathbf{v} \rangle}{c_0^2}\right)\mathbf{Id} + \frac{1}{c_0^2}\mathbf{v} \otimes \mathbf{v}\right) \cdot \mathbf{B} - \varepsilon_0\mathbf{E} \times \mathbf{v} \tag{2.79}$$

and expresses the Lorentz-invariance of $\mathbf{H}$ (*c.f.* [5, p. 323]). However, for $||\mathbf{v}|| \ll c_0$ one has the well known approximation

$$\mathbf{D} = \varepsilon_0\mathbf{E} + \varepsilon_0\mathbf{v} \times \mathbf{B} \tag{2.80}$$

$$\mathbf{H} = \frac{1}{\mu_0}\mathbf{B} + \varepsilon_0\mathbf{v} \times \mathbf{E}. \tag{2.81}$$

The first set of Maxwell equations are then obtained from equations (2.60) and (2.61) with above definitions,

$$\nabla \cdot \mathbf{D} = n^{\mathrm{F}} \qquad \mathbf{x} \in \Omega, \qquad [\![\mathbf{D}^{\mathrm{T}}]\!] \cdot \mathbf{n} = \underset{\mathrm{s}}{n}^{\mathrm{F}} \qquad \mathbf{x} \in \Sigma, \tag{2.82}$$

$$\nabla \cdot \mathbf{B} = 0 \qquad \mathbf{x} \in \Omega, \qquad [\![\mathbf{B}^{\mathrm{T}}]\!] \cdot \mathbf{n} = 0 \qquad \mathbf{x} \in \Sigma. \tag{2.83}$$

Clearly, the second set of Maxwell equations are obtained from equations (2.64), (2.65), (2.66) and (2.67),

$$\frac{\partial \mathbf{D}}{\partial t} = \frac{1}{\mu_0}\mathrm{curl}\,(\mathbf{B}) - n^{\mathrm{F}} \cdot \mathbf{v} - \mathbf{j}^{\mathrm{F}} \qquad \mathbf{x} \in \Omega \tag{2.84}$$

$$\underset{\mathrm{s}}{\mathbf{j}}^{\mathrm{F}} = \frac{1}{\mu_0}[\![\mathbf{B}]\!] \qquad \mathbf{x} \in \Sigma \tag{2.85}$$

and

$$\frac{\partial \mathbf{B}}{\partial t} = -\frac{1}{\varepsilon_0}\mathrm{curl}\,(\mathbf{D}) \qquad \mathbf{x} \in \Omega \tag{2.86}$$

$$\mathbf{0} = \frac{1}{\varepsilon_0}[\![\mathbf{D}]\!] \qquad \mathbf{x} \in \Sigma. \tag{2.87}$$

It is worth noting, that these apparently *simple* relationships are still coupled to $\mathbf{E}$ and $\mathbf{H}$ through the *complicated* Maxwell–Lorentz relation. Nevertheless, one could use the **Ansatz**

$$\frac{1}{\varepsilon_0}\mathbf{D} = -\nabla\Phi - \frac{\partial \mathbf{A}}{\partial t} \tag{2.88}$$

$$\mathbf{B} = \mathrm{curl}\,\mathbf{A} \tag{2.89}$$

in **moving** geometries to actually solve the equation system for a given charge and current density. Note, however, that Φ is the (electric) potential of $\frac{1}{\varepsilon_0}\mathbf{D}$ and **not** necessarily of $\mathbf{E}$. In the electrostatic limit, *i.e.* $\mathbf{A} \approx \mathbf{0}$, one obtains from equation (2.82) the **Poisson equation**

$$\varepsilon_0 \mathrm{div}\,\nabla\Phi = n^{\mathrm{F}} \tag{2.90}$$

if no polarization effects are present.

2.2.3 Polarization and magnetization

Beside free charge densities n^{F}, which are (linearly) related to the mass densities ρ_α, polarization or bounded charge arises. Briefly speaking, this covers all charge effects below the continuum mechanical point approximation, *e.g.* the dipole of water, which are not explicitly resolved in this framework. Since the bounded dipole charge arises from a microscopic dipole moment $\mathbf{p}$ one introduces the polarization (density) $\mathbf{P}$ as

$$\mathbf{P} = n\mathbf{p}, \tag{2.91}$$

where n is the number density of dipoles. In a mixture, however, on would introduce the species specific polarization $\mathbf{P}_\alpha$, arising from the (different) microscopic dipole moments $\mathbf{p}_\alpha$ and thus

$$\mathbf{P}_\alpha = n_\alpha \mathbf{p}_\alpha \tag{2.92}$$

$$\mathbf{P} := \sum_{\alpha=1}^{\mathrm{n}} n_\alpha \mathbf{p}_\alpha = \sum_{\alpha=1}^{\mathrm{n}} c_\alpha \mathbf{P}_\alpha. \tag{2.93}$$

If such a microscopic dipole is *cut* by a singular surface, (bounded) charge on either side of the surface arises, which is stated by the following assumption.

Assumption 6 (Polarization and bounded charge)**.**

The polarization (of each species) is assumed to be the origin of bounded charge in the sense that there exist (unique) densities $n^{\mathrm{B}}(\mathbf{x}, t)$ and $\underset{\mathrm{s}}{n}^{\mathrm{B}}(\mathbf{x}, t)$[5] such that

$$-\int_{\partial\Omega} \mathbf{P}_\alpha^{\mathrm{T}} \cdot d\mathbf{A} = \int_{\Omega} n^{\mathrm{B}}\, dV + \int_{\Sigma} \underset{\mathrm{s}}{n}^{\mathrm{B}}\, dA, \tag{2.94}$$

[5] On a singular surface Σ surface dipoles may occur [14], *e.g.* due to the adsorption of H_2O.

and for which the continuum hypothesis hold. The local relationships between polarization and bound charge are thus

$$-\operatorname{div}\mathbf{P} = n^{\mathrm{B}} \qquad \text{and} \qquad -[\![\mathbf{P}]\!]\cdot\mathbf{n} = \underset{\mathrm{s}}{n}^{\mathrm{B}}. \tag{2.95}$$

With this, the overall amount of charge in domain Ω containing a singular surface Σ is

$$Q = \int_{\Omega} n^{\mathrm{F}} + n^{\mathrm{B}}\, dV + \int_{\Sigma} \underset{\mathrm{s}}{n}^{\mathrm{F}} + \underset{\mathrm{s}}{n}^{\mathrm{B}}\, dA \tag{2.96}$$

$$= \int_{\Omega} n^{\mathrm{F}}\, dV + \int_{\Sigma} \underset{\mathrm{s}}{n}^{\mathrm{F}}\, dA - \oint_{\partial\Omega} \mathbf{P}^{\mathrm{T}}\cdot d\mathbf{A} - \int_{\Sigma} [\![\mathbf{P}]\!]\cdot d\mathbf{A}. \tag{2.97}$$

The bound charge may thus also produce an electric current $\mathbf{j}^{\mathrm{B}}$ (polarization current), according to

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Omega} n^{\mathrm{B}}\, dV = -\oint_{\partial\Omega} \mathbf{j}^{\mathrm{B}}\cdot\mathbf{A} \tag{2.98}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\Omega} \underset{\mathrm{s}}{n}^{\mathrm{B}}\, dA = -\oint_{\partial\Sigma} \underset{\mathrm{s}}{\mathbf{j}}^{\mathrm{B}}\cdot\mathbf{A}. \tag{2.99}$$

Due to the continuum hypothesis one deduces the explicit relationships

$$\mathbf{j}^{\mathrm{B}} = \frac{\partial\,\mathbf{P}}{\partial\,t} + \operatorname{curl}(\mathbf{P}\times\mathbf{v}) + (\operatorname{div}\mathbf{P})\cdot\mathbf{v} \tag{2.100}$$

$$\underset{\mathrm{s}}{\mathbf{j}}^{\mathrm{B}} = [\![\mathbf{P}\times\mathbf{v}]\!] \tag{2.101}$$

from the local flux balance equation (1.167). If the domain is at rest ($\mathbf{v} = 0$), the *origin* of a polarization current is a transient polarization field (*i.e.* $\mathbf{P} = \mathbf{P}(t)$).

Quite similar to polarization, the magnetization $\mathbf{M}$ is introduced. I will not derive magnetization in detail and refer to the classical textbooks on electrodynamics, *e.g. Classical Electrodynamics* by J. D. Jackson [15]. It is introduced here as the vector flux of some current $\mathbf{j}^{\mathrm{M}}$, called magnetization current. For an arbitrary surface $\sigma \in \Omega$ the magnetization obeys

$$\int_{\sigma} \left\langle \mathbf{j}^{\mathrm{M}},\, d\mathbf{A} \right\rangle = \int_{\partial\sigma} \mathbf{M}^{\mathrm{T}}\cdot d\mathbf{A} \tag{2.102}$$

and thus in local form

$$\mathbf{j}^{\mathrm{M}} = \operatorname{curl}\mathbf{M}. \tag{2.103}$$

Identifying the overall charge n^{Q} (and $\underset{\mathrm{s}}{n}^{\mathrm{Q}}$) and current $\mathbf{j}^{\mathrm{Q}}$ (and $\underset{\mathrm{s}}{\mathbf{j}}^{\mathrm{Q}}$) as

$$n^{\mathrm{Q}} := n^{\mathrm{F}} + n^{\mathrm{B}} \qquad \underset{\mathrm{s}}{n}^{\mathrm{Q}} := \underset{\mathrm{s}}{n}^{\mathrm{F}} + \underset{\mathrm{s}}{n}^{\mathrm{B}} \tag{2.104}$$

$$\mathbf{j}^{\mathrm{Q}} := \mathbf{j}^{\mathrm{F}} + \mathbf{j}^{\mathrm{B}} + \mathbf{j}^{\mathrm{M}} \qquad \underset{\mathrm{s}}{\mathbf{j}}^{\mathrm{Q}} := \underset{\mathrm{s}}{\mathbf{j}}^{\mathrm{F}} + \underset{\mathrm{s}}{\mathbf{j}}^{\mathrm{B}} \tag{2.105}$$

one could reconsider the coupled balance equation system (2.60)-(2.67). With the introduction of polarization and magnetization, the choice

$$a = n^{\mathrm{Q}} \qquad \underset{\mathrm{s}}{a} = n^{\mathrm{Q}} \tag{2.106}$$

$$\mathbf{j}_a = \mathbf{j}^{\mathrm{Q}} \qquad \underset{\mathrm{s}}{\mathbf{j}_a} = \underset{\mathrm{s}}{\mathbf{j}^{\mathrm{Q}}} \tag{2.107}$$

$$\mathbf{b} = \mathbf{D} \qquad \mathbf{c} = \mathbf{B} \tag{2.108}$$

$$\mathbf{j}_{\mathbf{b}} = \mathbf{H} \qquad \mathbf{j}_{\mathbf{c}} = -\mathbf{E} \tag{2.109}$$

explains $\mathbf{D}$ as potential of *any* (electric) charge and $\mathbf{H}$ as potential of *any* current, which are still subject to the Maxwell–Lorentz relation. One obtains thus the set of equations

$$\nabla \cdot \mathbf{D} = n^{\mathrm{Q}} \qquad [\![\mathbf{D}^{\mathrm{T}}]\!] \cdot \mathbf{n} = \underset{\mathrm{s}}{n^{\mathrm{Q}}} \tag{2.110}$$

$$\nabla \cdot \mathbf{B} = 0 \qquad [\![\mathbf{B}^{\mathrm{T}}]\!] \cdot \mathbf{n} = 0 \tag{2.111}$$

$$\frac{\partial \mathbf{D}}{\partial t} = \frac{1}{\mu_0} \operatorname{curl} \mathbf{B} - n^{\mathrm{Q}} \cdot \mathbf{v} - \mathbf{j}^{\mathrm{Q}} \qquad \frac{1}{\mu_0} [\![\mathbf{B}]\!] = \underset{\mathrm{s}}{\mathbf{j}^{\mathrm{Q}}} \tag{2.112}$$

$$\frac{\partial \mathbf{B}}{\partial t} = -\frac{1}{\varepsilon_0} \operatorname{curl} \mathbf{D} \qquad [\![\mathbf{D}]\!] = 0 \tag{2.113}$$

which are called **microscopic Maxwell equations**[6]. However, with the knowledge

$$n^{\mathrm{B}} = -\operatorname{div} \mathbf{P} \tag{2.114}$$

$$\mathbf{j}^{\mathrm{B}} = \frac{\partial \mathbf{P}}{\partial t} + \operatorname{curl} (\mathbf{P} \times \mathbf{v}) + (\operatorname{div} \mathbf{P}) \cdot \mathbf{v} \tag{2.115}$$

$$\mathbf{j}^{\mathrm{M}} = \operatorname{curl} \mathbf{M} \tag{2.116}$$

one could rewrite the set of equations as

$$\nabla \cdot (\mathbf{D} + \mathbf{P}) = n^{\mathrm{F}} \qquad [\![\mathbf{D} + \mathbf{P}]\!] \cdot \mathbf{n}^{\mathrm{T}} = \underset{\mathrm{s}}{n^{\mathrm{F}}} \tag{2.117}$$

$$\nabla \cdot \mathbf{B} = 0 \qquad [\![\mathbf{B}]\!] \cdot \mathbf{n}^{\mathrm{T}} = 0 \tag{2.118}$$

$$\frac{\partial (\mathbf{D} + \mathbf{P})}{\partial t} = \operatorname{curl} \left(\frac{1}{\mu_0} \mathbf{B} - \mathbf{M} - \mathbf{P} \times \mathbf{v}\right) - n^{\mathrm{F}} \cdot \mathbf{v} - \mathbf{j}^{\mathrm{F}},$$

$$[\![\frac{1}{\mu_0} \mathbf{B} - \mathbf{M} - \mathbf{P} \times \mathbf{v}]\!] = \underset{\mathrm{s}}{\mathbf{j}^{\mathrm{F}}} \tag{2.119}$$

$$\frac{\partial \mathbf{B}}{\partial t} = -\frac{1}{\varepsilon_0} \operatorname{curl} \mathbf{D} \qquad [\![\mathbf{D}]\!] = 0 \tag{2.120}$$

which are the final **macroscopic Maxwell equations**.

Remark 5 (Electric- and magnetic susceptibility).

A common assumption for simple, isotropic materials is a linear proportionality of polarization and magnetization to the electric and magnetic flux density, respectively, *i.e.*

$$\mathbf{P} = \chi^P \mathbf{D} = \varepsilon_0 \chi^P \mathbf{E} \tag{2.121}$$

$$\mathbf{M} = \chi^M \mathbf{H} = \frac{1}{\mu_0} \chi^M \mathbf{B}, \tag{2.122}$$

where χ^P and χ^M are called electric- and magnetic susceptibility. For a mixture (*c.f.* eq.

[6]Note that the term *microscopic* does not mean here an actual resolution of the charge densities.

2.93), however, one would accordingly choose

$$\mathbf{P}_\alpha = \varepsilon_0 \chi_\alpha^P \, \mathbf{E} \tag{2.123}$$

and thus

$$\mathbf{P} = \varepsilon_0 \left(\sum_{\alpha=1}^{\mathrm{n}} c_\alpha(\mathbf{x}, t) \chi_\alpha^P \right) \mathbf{E}. \tag{2.124}$$

Note, however, that an explicit relationship between $\mathbf{P}$ and $\mathbf{E}$ (and similar for $\mathbf{M}$ and $\mathbf{B}$) such as (2.121) and (2.124) are already **material specific** phenomenological relationships and thus **not** general. Such relationships are stated in the material modeling section 2.9.2 and necessary conditions derived via the entropy principle. In general $\mathbf{P}$ and $\mathbf{M}$ are yet unknown, arbitrary vector fields.

Next, the momentum and energy of the electromagnetic field will be discussed in order to formulate local conservation laws of total momentum and energy.

2.2.4 Momentum of the electromagnetic field

The electromagnetic momentum $\mathbf{p}_{\mathrm{EM}}$ of a domain Ω is [15]

$$\vec{p}_{\mathrm{EM}} = \int_\Omega \mathbf{D} \times \mathbf{B} \, dV \tag{2.125}$$

and

$$\mathbf{D} \times \mathbf{B} =: \mathbf{p}_{\mathrm{EM}} \tag{2.126}$$

is called momentum density of the electromagnetic field. This is Abraham's definition of the electromagnetic momentum[16]. In many other textbooks Abraham's momentum is written as $\mathbf{E} \times \mathbf{H}$, which is, however, only true for a system at rest due to the Maxwell–Lorentz relations.

With the set of Maxwell equations (2.110) - (2.113) it is possible to derive an explicit representations of

$$\frac{\partial \, \mathbf{p}_{\mathrm{EM}}}{\partial \, t} = -\mathrm{Div} \, \boldsymbol{\tau}_{\mathrm{EM}} + \mathbf{r}_{p_{\mathrm{EM}}}, \tag{2.127}$$

i.e. to cast the electromagnetic momentum variation into a balance equation, with the Maxwell stress tensor $\boldsymbol{\tau}_{\mathrm{EM}}$ and the source of electromagnetic momentum $\mathbf{r}_{p_{\mathrm{EM}}}$.

With the auxiliary calculations below one obtains

$$\begin{aligned} \frac{\partial \mathbf{D} \times \mathbf{B}}{\partial t} =& \mathrm{Div} \left(\frac{1}{\varepsilon_0} \mathbf{D} \otimes \mathbf{D} + \frac{1}{\mu_0} \mathbf{B} \otimes \mathbf{B} - \frac{1}{2} \left(\left\langle \frac{1}{\varepsilon_0} \mathbf{D}, \mathbf{D} \right\rangle + \left\langle \frac{1}{\mu_0} \mathbf{B}, \mathbf{B} \right\rangle \right) \cdot \mathbf{Id} \right) \\ & - n^{\mathrm{Q}} \cdot (\frac{1}{\varepsilon_0} \mathbf{D} + \mathbf{v} \times \mathbf{B}) - \mathbf{j}^{\mathrm{Q}} \times \mathbf{B}. \end{aligned} \tag{2.128}$$

Auxiliary calculation 2.13:

Multiplication of eq. (2.113) with $\mathbf{D}$ leads to

$$\begin{aligned}\frac{\partial \mathbf{B}}{\partial t} \times \mathbf{D} &= -\operatorname{curl}\left(\frac{1}{\varepsilon_0}\mathbf{D}\right) \times \mathbf{D} \\ \overset{\text{eq. }(A.39)}{=} &- \operatorname{Div}\left(\frac{1}{\varepsilon_0}\mathbf{D}\otimes\mathbf{D} - \frac{1}{2}\left\langle\frac{1}{\varepsilon_0}\mathbf{D},\mathbf{D}\right\rangle\cdot\mathbf{Id}\right) + (\operatorname{div}\mathbf{D})\cdot\frac{1}{\varepsilon_0}\mathbf{D} \\ = &- \operatorname{Div}\left(\frac{1}{\varepsilon_0}\mathbf{D}\otimes\mathbf{D} - \frac{1}{2}\left\langle\frac{1}{\varepsilon_0}\mathbf{D},\mathbf{D}\right\rangle\cdot\mathbf{Id}\right) + n^{\mathrm{Q}}\frac{1}{\varepsilon_0}\mathbf{D}\end{aligned}$$

Multiplication of eq. (2.112) with $\mathbf{B}$ obeys

$$\begin{aligned}\frac{\partial \mathbf{D}}{\partial t} \times \mathbf{B} &= \operatorname{curl}\left(\frac{1}{\mu_0}\mathbf{B}\right) \times \mathbf{B} - n^{\mathrm{Q}}\,\mathbf{v}\times\mathbf{B} - \mathbf{j}^{\mathrm{Q}}\times\mathbf{B} \\ &= \operatorname{Div}\left(\frac{1}{\mu_0}\mathbf{B}\otimes\mathbf{B} - \frac{1}{2}\left\langle\frac{1}{\mu_0}\mathbf{B},\mathbf{B}\right\rangle\cdot\mathbf{Id}\right) + n^{\mathrm{Q}}\,\mathbf{B}\times\mathbf{v} - \mathbf{j}^{\mathrm{Q}}\times\mathbf{B}\end{aligned}$$

A comparison to eq. (2.127) leads to the explicit representations of the EM-stress tensor and the EM-momentum source as

$$\boldsymbol{\tau}_{\mathrm{EM}} = -\left(\frac{1}{\varepsilon_0}\mathbf{D}\otimes\mathbf{D} + \frac{1}{\mu_0}\mathbf{B}\otimes\mathbf{B}) - \frac{1}{2}(\left\langle\varepsilon_0^{-1}\mathbf{D},\mathbf{D}\right\rangle + \left\langle\mu_0^{-1}\mathbf{B},\mathbf{B}\right\rangle)\cdot\mathbf{Id}\right) \tag{2.129}$$

$$\mathbf{r}_{p_{\mathrm{EM}}} = -n^{\mathrm{Q}}(\frac{1}{\varepsilon_0}\mathbf{D} + \mathbf{v}\times\mathbf{B}) - \mathbf{j}^{\mathrm{Q}}\times\mathbf{B} \tag{2.130}$$

Since the flux and source of momentum are now derived, the jump conditions of surface balance equation (*c.f.* 1.183) is used straight forward to derive the **electromagnetic momentum jump condition**

$$[\![\boldsymbol{\tau}_{\mathrm{EM}}]\!]\cdot\mathbf{n} = \underset{\mathrm{s}}{n}^{\mathrm{Q}}[\![\mathbf{E}]\!] + \underset{\mathrm{s}}{\mathbf{j}}^{\mathrm{Q}}\times[\![\mathbf{B}]\!]. \tag{2.131}$$

Note that in the momentum balance eq. (2.127) the overall charge density n^{Q} and current density $\mathbf{j}^{\mathrm{Q}}$ are present. Exploiting again the special relationships (eqs. (2.114), (2.115) and (2.116)) of the polarization $\mathbf{P}$ and magnetization $\mathbf{M}$ one could rewrite the EM momentum source $\mathbf{r}_{p_{\mathrm{EM}}}$ as

$$\begin{aligned}\mathbf{r}_{p_{\mathrm{EM}}} = &- n^{\mathrm{F}}(\frac{1}{\varepsilon_0}\mathbf{D} + \mathbf{v}\times\mathbf{B}) - \mathbf{j}^{\mathrm{F}}\times\mathbf{B} \\ &+ \operatorname{Div}\left(\frac{1}{\varepsilon_0}\mathbf{D}\otimes\mathbf{P} - \mathbf{B}\otimes\mathbf{M} - \frac{1}{2}\left(\left\langle\frac{1}{\varepsilon_0}\mathbf{D},\mathbf{P}\right\rangle - \langle\mathbf{B},\mathbf{M}\rangle\right)\mathbf{Id}\right) \\ &- \frac{1}{2}\left(\frac{1}{\varepsilon_0}\boldsymbol{\nabla}\mathbf{D}\cdot\mathbf{P} - \frac{1}{\varepsilon_0}\boldsymbol{\nabla}\mathbf{P}\cdot\mathbf{D}\right) - \frac{1}{2}\left((\boldsymbol{\nabla}\mathbf{B})\cdot\mathbf{M} - (\boldsymbol{\nabla}\mathbf{M})\cdot\mathbf{B}\right) \\ &- \left(\frac{\partial\mathbf{P}}{\partial t} + \operatorname{curl}(\mathbf{P}\times\mathbf{v})\right)\times\mathbf{B}.\end{aligned} \tag{2.132}$$

Auxiliary calculation 2.14:

$$
\begin{aligned}
(\operatorname{curl}\mathbf{M})\times\mathbf{B} &= \operatorname{Div}\left(\mathbf{B}\otimes\mathbf{M}-\langle\mathbf{B},\mathbf{M}\rangle\right)+(\boldsymbol{\nabla}\mathbf{B})\cdot\mathbf{M}\\
&= \operatorname{Div}\left(\mathbf{B}\otimes\mathbf{M}-\frac{1}{2}\langle\mathbf{B},\mathbf{M}\rangle\,\mathbf{Id}\right)+\frac{1}{2}\left((\boldsymbol{\nabla}\mathbf{B})\cdot\mathbf{M}-\boldsymbol{\nabla}\mathbf{M}\cdot\mathbf{B}\right)
\end{aligned}
$$

Auxiliary calculation 2.15:

$$
\begin{aligned}
&n^{\mathrm{B}}(\frac{1}{\varepsilon_0}\mathbf{D}+\mathbf{v}\times\mathbf{B})+\mathbf{j}^{\mathrm{B}}\times\mathbf{B}=n^{\mathrm{B}}\frac{1}{\varepsilon_0}\mathbf{D}+\left(\frac{\partial\mathbf{P}}{\partial t}+\operatorname{curl}(\mathbf{P}\times\mathbf{v})\right)\times\mathbf{B}\\
&=-\operatorname{Div}(\frac{1}{\varepsilon_0}\mathbf{D}\otimes\mathbf{P})+\frac{1}{\varepsilon_0}(\boldsymbol{\nabla}\mathbf{D})\cdot\mathbf{P}+\left(\frac{\partial\mathbf{P}}{\partial t}+\operatorname{curl}(\mathbf{P}\times\mathbf{v})\right)\times\mathbf{B}\\
&=-\operatorname{Div}\left(\frac{1}{\varepsilon_0}\mathbf{D}\otimes\mathbf{P}-\frac{1}{2}\left\langle\frac{1}{\varepsilon_0}\mathbf{D},\mathbf{P}\right\rangle\mathbf{Id}\right)+\frac{1}{2}\left(\frac{1}{\varepsilon_0}\boldsymbol{\nabla}\mathbf{D}\cdot\mathbf{P}-\frac{1}{\varepsilon_0}\boldsymbol{\nabla}\mathbf{P}\cdot\mathbf{D}\right)\\
&\qquad+\left(\frac{\partial\mathbf{P}}{\partial t}+\operatorname{curl}(\mathbf{P}\times\mathbf{v})\right)\times\mathbf{B}
\end{aligned}
$$

One could thus reconsider the partition of eq. (2.128) in a balance equation. Shifting the second term of (2.132) to the EM-stress tensor leads to an (equal) **alternative** balance equation

$$
\frac{\partial\,\mathbf{D}\times\mathbf{B}}{\partial t}=-\operatorname{Div}\boldsymbol{\tau}_{\mathrm{PM}}+\mathbf{r}_{p_{\mathrm{PM}}},\tag{2.133}
$$

with

$$
\boldsymbol{\tau}_{\Delta}:=\frac{1}{\varepsilon_0}\mathbf{D}\otimes\mathbf{P}-\mathbf{B}\otimes\mathbf{M}-\frac{1}{2}\left(\left\langle\frac{1}{\varepsilon_0}\mathbf{D},\mathbf{P}\right\rangle-\langle\mathbf{B},\mathbf{M}\rangle\right)\mathbf{Id}\tag{2.134}
$$

$$
\begin{aligned}
\boldsymbol{\tau}_{\mathrm{PM}}&:=\boldsymbol{\tau}_{\mathrm{EM}}+\boldsymbol{\tau}_{\Delta}\qquad(2.135)\\
&=\frac{1}{\varepsilon_0}\mathbf{D}\otimes(\mathbf{D}+\mathbf{P})+\mathbf{B}\otimes(\frac{1}{\mu_0}\mathbf{B}-\mathbf{M})-\frac{1}{2}\left(\left\langle\frac{1}{\varepsilon_0}\mathbf{D},\mathbf{D}+\mathbf{P}\right\rangle+\left\langle\mathbf{B},\frac{1}{\mu_0}\mathbf{B}-\mathbf{M}\right\rangle\right)\mathbf{Id}\\
\mathbf{r}_{p_{\mathrm{PM}}}&=-n^{\mathrm{F}}(\frac{1}{\varepsilon_0}\mathbf{D}+\mathbf{v}\times\mathbf{B})-\mathbf{j}^{\mathrm{F}}\times\mathbf{B}-\left(\frac{\partial\mathbf{P}}{\partial t}+\operatorname{curl}(\mathbf{P}\times\mathbf{v})\right)\times\mathbf{B}\\
&\quad\underbrace{-\frac{1}{2}(\varepsilon_0^{-1}\boldsymbol{\nabla}\mathbf{D}\cdot\mathbf{P}-\varepsilon_0^{-1}\boldsymbol{\nabla}\mathbf{P}\cdot\mathbf{D}+\boldsymbol{\nabla}\mathbf{B}\cdot\mathbf{M}-\boldsymbol{\nabla}\mathbf{M}\cdot\mathbf{B})}_{=:\mathbf{g}_{\mathrm{PM}}}.\qquad(2.136)
\end{aligned}
$$

The abbreviation $\mathbf{g}_{\mathrm{PM}}$ is quite useful as $\mathbf{g}_{\mathrm{PM}}$ vanishes in linear materials, *i.e.* if $\mathbf{P}=\chi^P\mathbf{D}$ and $\mathbf{M}=\chi^M\mathbf{B}$, with constants χ^P and χ^M.
Central behind this derivation is the conversion

$$
n^{\mathrm{B}}\cdot\mathbf{D}+\mathbf{j}^{\mathrm{M}}\times\mathbf{B}=-\operatorname{Div}\boldsymbol{\tau}_{\Delta}+\mathbf{g}_{\mathrm{PM}}.\tag{2.137}
$$

This alternative representation of the electromagnetic momentum balance lead to a quite outstanding confusion, which is briefly discussed in the following remark.

Remark 6 (Abraham–Minkowski dilemma).

One might ask if the definition of the electromagnetic momentum in polarized media is

satisfactory. From the viewpoint of the macroscopic Maxwell equations, one could imagine also $(\mathbf{D}+\mathbf{P})\times\mathbf{B}$ as momentum definition. This question arose already at the beginning of 20th century where Abraham [16] defined (in my notation),

$$\mathbf{D}\times\mathbf{B} \tag{2.138}$$

as electromagnetic momentum and Hermann Minkowski (1910) [17] chose the definition

$$(\mathbf{D}+\mathbf{P})\times\mathbf{B}. \tag{2.139}$$

This controversy was of course quite often discussed (see *e.g.* [18–20]) and is **still** ongoing, as the recent publication "Resolution of the Abraham-Minkowski Dilemma" (S. M. Barnett, Phys. Rev. Lett., 2010, [21]) suggests. However, there is still doubt on the exact definition and, surprisingly, and experimental verification is not as simple as one might think.

Nevertheless, I will also briefly discuss this dilemma in my notation. The following two auxiliary calculations are quite useful.

Auxiliary calculation 2.16:

Multiplication of eq. (2.113) with $\mathbf{D}$ leads to

$$\begin{aligned}
\frac{\partial\mathbf{B}}{\partial t}\times(\mathbf{D}+\mathbf{P}) &= -\operatorname{curl}\left(\frac{1}{\varepsilon_0}\mathbf{D}\right)\times(\mathbf{D}+\mathbf{P})\\
&\overset{\text{eq. }(A.39)}{=} -\operatorname{Div}\left(\frac{1}{\varepsilon_0}\mathbf{D}\otimes(\mathbf{D}+\mathbf{P})-\frac{1}{2}\left\langle\frac{1}{\varepsilon_0}\mathbf{D},(\mathbf{D}+\mathbf{P})\right\rangle\cdot\mathbf{Id}\right)\\
&\quad+\operatorname{div}(\mathbf{D}+\mathbf{P})\cdot\frac{1}{\varepsilon_0}\mathbf{D}-\frac{1}{2}\frac{1}{\varepsilon_0}(\boldsymbol{\nabla}(\mathbf{D}+\mathbf{P})\cdot\mathbf{D}-\boldsymbol{\nabla}\mathbf{D}\cdot(\mathbf{D}+\mathbf{P}))\\
&= -\operatorname{Div}\left(\frac{1}{\varepsilon_0}\mathbf{D}\otimes(\mathbf{D}+\mathbf{P})-\frac{1}{2}\left\langle\frac{1}{\varepsilon_0}\mathbf{D},(\mathbf{D}+\mathbf{P})\right\rangle\cdot\mathbf{Id}\right)\\
&\quad+n^{\mathrm{F}}\cdot\frac{1}{\varepsilon_0}\mathbf{D}-\frac{1}{2}\frac{1}{\varepsilon_0}(\boldsymbol{\nabla}\mathbf{P}\cdot\mathbf{D}-\boldsymbol{\nabla}\mathbf{D}\cdot\mathbf{P})
\end{aligned}$$

Auxiliary calculation 2.17:

Multiplication of eq. (2.112) with $\mathbf{B}$ obeys

$$\begin{aligned}
\frac{\partial\,\mathbf{D}+\mathbf{P}}{\partial\,t}\times\mathbf{B} &= \left(\operatorname{curl}(\mu_0^{-1}\mathbf{B}-\mathbf{M})\right)\times\mathbf{B}-n^{\mathrm{F}}\,\mathbf{v}\times\mathbf{B}-\mathbf{j}^{\mathrm{F}}\times\mathbf{B}\\
&= \operatorname{Div}\left(\mathbf{B}\otimes(\mu_0^{-1}\mathbf{B}-\mathbf{M})-\frac{1}{2}\left\langle\mathbf{B},(\mu_0^{-1}\mathbf{B}-\mathbf{M})\right\rangle\cdot\mathbf{Id}\right)\\
&\quad+n^{\mathrm{F}}\,\mathbf{B}\times\mathbf{v}-\mathbf{j}^{\mathrm{F}}\times\mathbf{B}\\
&\quad+\frac{1}{2}\left(\boldsymbol{\nabla}\mathbf{B}\cdot(\mu_0^{-1}\mathbf{B}-\mathbf{M})-\boldsymbol{\nabla}(\mu_0^{-1}\mathbf{B}-\mathbf{M})\cdot\mathbf{B}\right)\\
&= \operatorname{Div}\left(\mathbf{B}\otimes(\mu_0^{-1}\mathbf{B}-\mathbf{M})-\frac{1}{2}\left\langle\mathbf{B},(\mu_0^{-1}\mathbf{B}-\mathbf{M})\right\rangle\cdot\mathbf{Id}\right)\\
&\quad+n^{\mathrm{F}}\,\mathbf{B}\times\mathbf{v}-\mathbf{j}^{\mathrm{F}}\times\mathbf{B}-\frac{1}{2}\left(\boldsymbol{\nabla}\mathbf{B}\cdot\mathbf{M}-\boldsymbol{\nabla}\mathbf{M}\cdot\mathbf{B}\right)
\end{aligned}$$

Considering now $(\mathbf{D}+\mathbf{P})\times\mathbf{B}$ one concludes

$$\frac{\partial\,(\mathbf{D}+\mathbf{P})\times\mathbf{B}}{\partial\,t} = \mathrm{Div}\left(\frac{1}{\varepsilon_0}\mathbf{D}\otimes(\mathbf{D}+\mathbf{P}) + \frac{1}{\mu_0}\mathbf{B}\otimes(\mu_0^{-1}\mathbf{B}-\mathbf{M})\right. \tag{2.140}$$

$$-\frac{1}{2}\left(\left\langle\frac{1}{\varepsilon_0}\mathbf{D},(\mathbf{D}+\mathbf{P})\right\rangle + \left\langle\mathbf{B},(\mu_0^{-1}\mathbf{B}-\mathbf{M})\right\rangle\right)\cdot\mathbf{Id}\Big) \tag{2.141}$$

$$-\,n^{\mathrm{F}}\cdot(\frac{1}{\varepsilon_0}\mathbf{D}+\mathbf{v}\times\mathbf{B}) + \frac{1}{2}\frac{1}{\varepsilon_0}(\boldsymbol{\nabla}\mathbf{P}\cdot\mathbf{D}-\boldsymbol{\nabla}\mathbf{D}\cdot\mathbf{P}) \tag{2.142}$$

$$+\frac{1}{2}(\boldsymbol{\nabla}\mathbf{B}\cdot\mathbf{M}-\boldsymbol{\nabla}\mathbf{M}\cdot\mathbf{B}) \tag{2.143}$$

$$= -\mathrm{Div}\,\boldsymbol{\tau}_{\mathrm{PM}} + \mathbf{r}_{p_{\mathrm{PM}}} + \left(\frac{\partial\,\mathbf{P}}{\partial\,t} + \mathrm{curl}\,(\mathbf{P}\times\mathbf{v})\right)\times\mathbf{B}. \tag{2.144}$$

This is remarkably, as the balance equation of $\mathbf{D}\times\mathbf{B}$ is quite similar to the one of $(\mathbf{D}+\mathbf{P})\times\mathbf{B}$, and also explains why a measurement is so difficult, since the actual difference between the two momentum definitions is

$$\left(\frac{\partial\,\mathbf{P}}{\partial\,t} + \mathrm{curl}\,(\mathbf{P}\times\mathbf{v})\right)\times\mathbf{B}. \tag{2.145}$$

However, I will *avoid the dilemma* with the following assumption.

Assumption 7 (Constant polarization current-magnetic force)**.**

Throughout the further work it is assumed that

$$\left(\frac{\partial\,\mathbf{P}}{\partial\,t} + \mathrm{curl}\,(\mathbf{P}\times\mathbf{v})\right)\times\mathbf{B} \equiv 0, \tag{2.146}$$

which is also motivated by $||\mathbf{v}|| \ll c_0$. This resolves in my work the Abraham–Minkowski dilemma, and the two electromagnetic momentum definitions coincide.

2.2.5 Field energy

Similar to the EM-momentum I refer to the work of Jackson[15], de Groot[10] and Müller[5] to an in-depth investigation of the field energy.

The **electromagnetic field energy** (or simply EM energy) is defined as

$$e_{\mathrm{EM}} = \frac{1}{2}\left(\varepsilon_0\mathbf{D}\cdot\mathbf{D}^{\mathrm{T}} + \mu_0\mathbf{B}\cdot\mathbf{B}^{\mathrm{T}}\right). \tag{2.147}$$

With auxiliary calculations 2.18 one obtains the **balance of electromagnetic field energy**

$$\frac{\partial e_{\mathrm{EM}}}{\partial t} = -\mathrm{div}\,(\mathbf{S}) - \varepsilon_0^{-1}\,(n^{\mathrm{Q}}\,\mathbf{v}+\mathbf{j}^{\mathrm{Q}})\cdot\mathbf{D}^{\mathrm{T}} \tag{2.148}$$

where

$$\mathbf{S} = c_0^2\mathbf{D}\times\mathbf{B} \tag{2.149}$$

is called flux of the electromagnetic field or **Poynting vector** and

$$-\varepsilon_0^{-1}\,(n^{\mathrm{Q}}\,\mathbf{v}+\mathbf{j}^{\mathrm{Q}})\cdot\mathbf{D}^{\mathrm{T}} = -\varepsilon_0^{-1}\,\mathbf{i}^{\mathrm{Q}}\cdot\mathbf{D}^{\mathrm{T}} \tag{2.150}$$

the sink (or source) of the field energy. Note again that the charge and flux densities are the overall ones, covering the contributions due to polarization and magnetization.

Auxiliary calculation 2.18:

$$\begin{aligned}
\operatorname{div}(\mathbf{D}\times\mathbf{B}) &\overset{\text{eq.}(A.41)}{=} (\operatorname{curl}\mathbf{D})\cdot\mathbf{B}^{\mathrm{T}} - (\operatorname{curl}\mathbf{B})\cdot\mathbf{D}^{\mathrm{T}} \\
&\overset{\text{eqs.}(2.112)\&(2.113)}{=} -\varepsilon_0\left(\frac{\partial\mathbf{B}}{\partial t}\right)\cdot\mathbf{B}^{\mathrm{T}} - \mu_0\left(\frac{\partial\mathbf{D}}{\partial t} + n^{\mathrm{Q}}\,\mathbf{v} + \mathbf{j}^{\mathrm{Q}}\right)\cdot\mathbf{D}^{\mathrm{T}} \\
&= -\frac{1}{c_0^2}\left(\mu_0\frac{\partial\mathbf{B}}{\partial t}\cdot\mathbf{B}^{\mathrm{T}} + \varepsilon_0\frac{\partial\mathbf{D}}{\partial t}\mathbf{D}^{\mathrm{T}}\right) - \mu_0\left(n^{\mathrm{Q}}\,\mathbf{v} + \mathbf{j}^{\mathrm{Q}}\right)\cdot\mathbf{D}^{\mathrm{T}}
\end{aligned}$$

This balance equation could again be rewritten in an alternative form, using the following auxiliary calculations.

Auxiliary calculation 2.19:

$$\begin{aligned}
\varepsilon_0^{-1}\,\mathbf{j}^{\mathrm{M}}\cdot\mathbf{D}^{\mathrm{T}} &= \varepsilon_0^{-1}\,(\operatorname{curl}M)\cdot\mathbf{D}^{\mathrm{T}} = -c_0^2\operatorname{div}(\mathbf{D}\times\mu_0\mathbf{M}) + (\operatorname{curl}\varepsilon_0^{-1}\mathbf{D})\cdot\mathbf{M}^{\mathrm{T}} \\
&= -c_0^2\operatorname{div}(\mathbf{D}\times\mu_0\mathbf{M}) - \frac{\partial\mathbf{B}}{\partial t}\cdot\mathbf{M}^{\mathrm{T}}
\end{aligned}$$

Auxiliary calculation 2.20:

$$\begin{aligned}
\varepsilon_0^{-1}\,(n^{\mathrm{B}}\,\mathbf{v} + \mathbf{j}^{\mathrm{B}})\cdot\mathbf{D}^{\mathrm{T}} &= \varepsilon_0^{-1}\left(\frac{\partial\mathbf{P}}{\partial t} + \operatorname{curl}(\mathbf{P}\times\mathbf{v})\right)\cdot\mathbf{D}^{\mathrm{T}} \\
&= \varepsilon_0^{-1}\,\frac{\partial\mathbf{P}}{\partial t}\cdot\mathbf{D}^{\mathrm{T}} - \frac{1}{c_0^2}\operatorname{div}(\mathbf{D}\times(\mu_0\mathbf{P}\times\mathbf{v})) - \frac{\partial\mathbf{B}}{\partial t}\cdot(\mathbf{P}\times\mathbf{v})^{\mathrm{T}} \\
&= -\frac{\partial\,\varepsilon_0^{-1}\mathbf{D}\cdot\mathbf{P}}{\partial t}\cdot\mathbf{D}^{\mathrm{T}} + \frac{\partial\,\varepsilon_0^{-1}\mathbf{D}}{\partial t}\cdot\mathbf{P} \\
&\quad - \frac{1}{c_0^2}\operatorname{div}(\mathbf{D}\times(\mu_0\mathbf{P}\times\mathbf{v})) - \frac{\partial\mathbf{B}}{\partial t}\cdot(\mathbf{P}\times\mathbf{v})^{\mathrm{T}}
\end{aligned}$$

Quite similar to the alternative balance equation of the electromagnetic momentum (eq. (2.133)), an **alternative field energy balance** equation is obtained,

$$\begin{aligned}
\frac{\partial(e_{\mathrm{EM}} + \mathbf{P}\cdot\mathbf{D})}{\partial t} &= -c_0^2\operatorname{div}(\mathbf{D}\times(\mathbf{B} - \mu_0(\mathbf{M} + \mathbf{P}\times\mathbf{v}))) - \mathbf{i}^{\mathrm{F}}\cdot\varepsilon_0^{-1}\mathbf{D}^{\mathrm{T}} \\
&\quad + \frac{\partial\mathbf{D}}{\partial t}\cdot\mathbf{P}^{\mathrm{T}} + \frac{\partial\mathbf{B}}{\partial t}\cdot(\mathbf{M} + \mathbf{P}\times\mathbf{v}).
\end{aligned} \tag{2.151}$$

The term

$$e_{\mathrm{PM}} := e_{\mathrm{EM}} + \mathbf{P}\cdot\mathbf{D} \tag{2.152}$$

is interpreted as the **electromagnetic field energy in polarizable media** and

$$\mathbf{S}_{\mathrm{PM}} := c_0^2\,\mathbf{D}\times(\mathbf{B} - \mu_0(\mathbf{M} + \mathbf{P}\times\mathbf{v})) \tag{2.153}$$

is called energy flux in polarize- and magnetizeable media.

2.3 Conservation of total momentum

The global definition of momentum, *i.e.*

$$\vec{p}_{\mathrm{M}} = M \cdot \vec{v}, \tag{2.154}$$

where M is the total mass of the body and $\vec{v}$ the velocity of its centre of mass, motivates the momentum density $\mathbf{p}_{\mathrm{M}}$ with

$$\vec{p}_{\mathrm{M}} = \int_{\Omega} \mathbf{p}_{\mathrm{M}}(\mathbf{x}, t)\, d\mathbf{x}. \tag{2.155}$$

Independent of the frame of reference, the momentum density is equal to the total mass flux, *i.e.*

$$\mathbf{p}_{\mathrm{M}} = \rho \mathbf{v} + \mathbf{j}. \tag{2.156}$$

Here it can again be seen why the standard coordinate system, implying $\mathbf{j}(\mathbf{x}, t) = 0$, is convenient, since it implies

$$\mathbf{p}_{\mathrm{M}}(\mathbf{x}, t) = \rho(\mathbf{x}, t)\, \mathbf{v}(\mathbf{x}, t). \tag{2.157}$$

If another Eulerian coordinate system $(\mathbf{y}, \overline{\mathbf{v}}))$ is chosen such that, *e.g.* $\sum_{\alpha=1}^{\mathrm{n}} m_\alpha \cdot \mathbf{j}_\alpha(\mathbf{y}, t) = 0$ and $\bar{\mathbf{j}}(\mathbf{y}, t) \neq 0$, the mass flux constraint 2.17 is used for the representation

$$\overline{\mathbf{p}}_{\mathrm{M}}(\mathbf{y}, t) = \overline{\rho}_{\mathrm{n}}(\mathbf{y}, t)\overline{\mathbf{v}}(\mathbf{y}, t) + \sum_{\alpha=1}^{\mathrm{n}} \mathbf{j}_\alpha(\mathbf{y}, t). \tag{2.158}$$

In an inertial frame of reference, Newtons second law classically states

$$\dot{\vec{p}} = \vec{F}, \tag{2.159}$$

where $\vec{F}$ is the force acting on the object. The continuum mechanical version is stated in the following assumption.

Assumption 8 (Newtons second law)**.**

In a continuum mechanical or field description the force acting on the body is supposed to consist of a flux and a source part, *i.e.*

$$\vec{F} = \vec{J}_F + \vec{R}_F \tag{2.160}$$

$$\vec{J}_F = -\oint_{\partial\Omega} \boldsymbol{\sigma}_{\mathrm{M}}^{\mathrm{T}}\, d\mathbf{A} \tag{2.161}$$

$$\vec{R}_F = \int_{\Omega} \mathbf{f}\, d\mathbf{x}, \tag{2.162}$$

where $\boldsymbol{\sigma}$ is called stress tensor and $\mathbf{f}$ the overall force density acting on body. Together with Reynolds transport theorem for vector fields, one obtains thus the **local version of Newtons second law** in the standard coordinate system

$$\frac{\partial \rho \mathbf{v}}{\partial t} = -\mathrm{Div}\ (\rho \mathbf{v} \otimes \mathbf{v} + \boldsymbol{\sigma}_{\mathrm{M}}) + \mathbf{f}. \tag{2.163}$$

Note, however, that the overall force density $\mathbf{f}$ is not yet specified, but *derived* from the following postulation.

Assumption 9 (Conservation of total momentum)**.**

The total momentum (in absence of gravitational effects) of a polarize- and magnetizeable media

$$\vec{p} = \vec{p}_{\mathrm{M}} + \vec{p}_{\mathrm{EM}} \tag{2.164}$$

is supposed to obey a global conservation equation, *i.e.*

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\int_{\Omega} \mathbf{p}_{\mathrm{M}} + \mathbf{p}_{\mathrm{EM}}\, d\mathbf{x}\right) \stackrel{!}{=} -\oint_{\Omega} \mathbf{J}_{\mathbf{p}}^{\mathrm{T}} \cdot d\mathbf{A} \tag{2.165}$$

with the total momentum flux $\mathbf{J}_{\mathbf{p}}$, and the continuum hypothesis.

Summing the local balance equations of electromagnetic momentum and material (eqs. 2.133 and (2.163)) leads to

$$\frac{\partial(\mathbf{p}_{\mathrm{M}} + \mathbf{p}_{\mathrm{EM}})}{\partial t} = -\mathrm{Div}\ (\rho\mathbf{v} \otimes \mathbf{v} + \boldsymbol{\sigma}_{\mathrm{M}} - \boldsymbol{\tau}_{\mathrm{EM}}) + \mathbf{f} + \mathbf{r}_{p_{\mathrm{EM}}}. \tag{2.166}$$

In comparison to the local momentum conservation

$$\frac{\partial \mathbf{p}}{\partial t} = -\mathrm{Div}\ (\mathbf{p} \otimes \mathbf{v} + \mathbf{J}_{\mathbf{p}}), \tag{2.167}$$

one thus deduces

$$\mathbf{f} = -\mathbf{r}_{p_{\mathrm{EM}}}. \tag{2.168}$$

At this point a discussion of the resulting relationships is quite interesting. The total momentum flux consists of the difference between the stress tensor of the material and the electromagnetic stress tensor. If the momentum flux is supposed to vanish ($\mathbf{J}_{\mathbf{p}} = 0$) then material stress is *balanced* by the field stress.
Further, the equation dictates the *shape* of the force density acting on (or within) the material. Expectably, the force density $\mathbf{f}$ is the local version of the Lorentz force (*i.e.* $\mathbf{f} = n^{\mathrm{F}}\,\mathbf{E} + \mathbf{j}^{\mathrm{F}} \times \mathbf{B}$) in addition to forces arising due to polarization and magnetization (ponderomotive force). The momentum balance of material (or Newtons second law eq. 2.163) is thus

$$\frac{\partial \rho\mathbf{v}}{\partial t} = -\ \mathrm{Div}\ (\rho\mathbf{v} \otimes \mathbf{v} + \boldsymbol{\sigma}) + \varepsilon_0^{-1} n^{\mathrm{F}}\,\mathbf{D} + \mathbf{j}^{\mathrm{F}} \times \mathbf{B} + \mathbf{g}_{\mathrm{PM}}, \tag{2.169}$$

where the effective stress tensor $\boldsymbol{\sigma}$ of material and polarization/magnetization

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{\mathrm{M}} - \frac{1}{\varepsilon_0}\mathbf{D} \otimes \mathbf{P} + \mathbf{B} \otimes \mathbf{M} + \frac{1}{2}\left(\left\langle \frac{1}{\varepsilon_0}\mathbf{D}, \mathbf{P}\right\rangle - \langle \mathbf{B}, \mathbf{M}\rangle\right)\mathbf{Id} = \boldsymbol{\sigma}_{\mathrm{M}} - \boldsymbol{\tau}_{\Delta} \tag{2.170}$$

is introduced, and further simply called **momentum balance**.

Definition 8 (Mechanical equilibrium)**.**

Following the terminology given in [10] a physical object is in **mechanical equilibrium**

iff

$$\frac{\partial \rho \mathbf{v}}{\partial t} + \mathrm{Div}\ (\rho \mathbf{v} \otimes \mathbf{v}) = 0. \tag{2.171}$$

From the viewpoint of global balance equations, this corresponds to

$$\frac{\mathrm{d}\vec{p}_{\mathrm{M}}}{\mathrm{d}t} = 0, \tag{2.172}$$

i.e. the system is **not accelerated**. Since this holds for many stationary or quasi-stationary systems it is a reasonable assumption for many situations. In accordance, the remaining momentum balance

$$\mathrm{Div}\, \boldsymbol{\sigma} = \varepsilon_0^{-1} n^{\mathrm{F}}\, \mathbf{D} + \mathbf{j}^{\mathrm{F}} \times \mathbf{B} + \mathbf{g}_{\mathrm{PM}} \tag{2.173}$$

is called **stationary momentum balance equation**.

Definition 9 (Pressure)**.**

Material or elastic pressure is p defined as

$$p := \frac{1}{3}\mathrm{tr}(\boldsymbol{\sigma}_{\mathrm{M}}) \tag{2.174}$$

and thus the decomposition

$$\boldsymbol{\sigma} = (p + \frac{1}{2}\varepsilon_0^{-1}\mathbf{D} \cdot \mathbf{P}^{\mathrm{T}} - \frac{1}{2}\mathbf{B} \cdot \mathbf{M}^{\mathrm{T}})\mathbf{Id} + \boldsymbol{\pi} - \frac{1}{\varepsilon_0}\mathbf{D} \otimes \mathbf{P} + \mathbf{B} \otimes \mathbf{M} \tag{2.175}$$

holds, where $\boldsymbol{\pi}_{\mathrm{M}}$ is called viscous stress tensor of the material and

$$\boldsymbol{\pi} := \boldsymbol{\pi}_{\mathrm{M}} - \frac{1}{\varepsilon_0}\mathbf{D} \otimes \mathbf{P} + \mathbf{B} \otimes \mathbf{M} \tag{2.176}$$

total viscous stress tensor. Reconsidering the definition of the material force flux through $\partial\Omega$, *i.e.*

$$\vec{J}_F = -\oint_{\partial\Omega} \boldsymbol{\sigma}_{\mathrm{M}}^{\mathrm{T}} \cdot\, d\mathbf{A} = \underbrace{-\oint_{\partial\Omega} p \cdot \mathbf{n}\, dA}_{=:\vec{J}_{F,p}} \underbrace{-\oint_{\partial\Omega} \boldsymbol{\pi}^{\mathrm{T}} \cdot\, d\mathbf{A}}_{=:\vec{J}_{F,\boldsymbol{\pi}}}, \tag{2.177}$$

leads to the conclusion that pressure generates only a force in normal direction of $\partial\Omega$. Note, however, that the pressure p is (yet) undetermined.

2.4 Conservation of energy

Quite similar to the local version of Newtons second law, a first law of thermodynamics will be assumed, stating that the total energy obeys a conservation equation. However, before this assumption is stated, some preliminary discussion on energy density is required.

The kinetic energy of the whole system is (quite similar to the momentum)

$$E_{\text{kin}} = \frac{1}{2} M \vec{v}^2 \tag{2.178}$$

where M is again the total mass and $\vec{v}$ the center of mass velocity. This gives rise to a **kinetic energy density**

$$e_{\text{M}} = \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v}^{\text{T}}. \tag{2.179}$$

The corresponding balance equation is obtained by multiplying the momentum balance eq. (2.169) with $\mathbf{v}^{\text{T}}$ and some vector calculus transformations (*c.f.* auxiliary calculation 2.21).

Auxiliary calculation 2.21: Kinetic energy density

$$\frac{\partial \frac{1}{2}\rho \mathbf{v} \cdot \mathbf{v}^{\text{T}}}{\partial t} = \frac{1}{2}\left(\frac{\partial \rho \mathbf{v}}{\partial t} \cdot \mathbf{v}^{\text{T}} + \frac{\partial \mathbf{v}}{\partial t} \rho \mathbf{v}^{\text{T}}\right) = \frac{\partial \rho \mathbf{v}}{\partial t} \cdot \mathbf{v}^{\text{T}} - \frac{1}{2}\frac{\rho}{t} \mathbf{v}\mathbf{v}^{\text{T}}.$$

Inserting the momentum and mass balance leads to

$$\begin{aligned}\frac{\partial \rho \mathbf{v}}{\partial t} \cdot \mathbf{v}^{\text{T}} - \frac{1}{2}\frac{\partial \rho}{\partial t} \mathbf{v}\mathbf{v}^{\text{T}} = &-\text{Div}\ (\rho \mathbf{v} \otimes \mathbf{v} + \boldsymbol{\sigma}_{\text{M}})\, \mathbf{v}^{\text{T}} + n^{\text{Q}}\, \mathbf{E} \cdot \mathbf{v}^{\text{T}} \\ &+ (\mathbf{j}^{\text{Q}} \times \mathbf{B}) \cdot \mathbf{v}^{\text{T}} + \frac{1}{2}\text{div}\,(\rho \mathbf{v}) \cdot \mathbf{v}\mathbf{v}^{\text{T}}.\end{aligned}$$

With relation (A.27) one deduces

$$-\text{Div}\ (\rho \mathbf{v} \otimes \mathbf{v} + \boldsymbol{\sigma}_{\text{M}})\, \mathbf{v}^{\text{T}} = -\text{div}\,(\rho(\mathbf{v} \otimes \mathbf{v}) \cdot \mathbf{v}^{\text{T}} + \boldsymbol{\sigma}_{\text{M}} \cdot \mathbf{v}^{\text{T}}) + (\rho \mathbf{v} \otimes \mathbf{v} + \boldsymbol{\sigma}_{\text{M}}) \bullet \boldsymbol{\nabla} \mathbf{v}$$

and according to (A.31)

$$\frac{1}{2}\text{div}\,(\rho \mathbf{v})\, \mathbf{v} \cdot \mathbf{v}^{\text{T}} = \text{div}\,\big(\frac{1}{2}(\rho \mathbf{v} \otimes \mathbf{v}) \cdot \mathbf{v}^{\text{T}}\big) - \frac{1}{2}\rho \mathbf{v} \cdot \nabla(\mathbf{v} \cdot \mathbf{v}^{\text{T}}).$$

Further, exploiting (A.25) and (A.32) one could rewrite

$$\frac{1}{2}\rho \mathbf{v} \cdot \nabla(\mathbf{v} \cdot \mathbf{v}^{\text{T}}) = (\rho \mathbf{v} \otimes \mathbf{v}) \bullet \boldsymbol{\nabla} \mathbf{v}$$

and thus

$$(\rho \mathbf{v} \otimes \mathbf{v}) \bullet \boldsymbol{\nabla} \mathbf{v} + \frac{1}{2}\text{div}\,(\rho \mathbf{v}) \cdot \mathbf{v}\mathbf{v}^{\text{T}} = \text{div}\,\big(\frac{1}{2}(\rho \mathbf{v} \otimes \mathbf{v}) \cdot \mathbf{v}^{\text{T}}\big).$$

Putting the intermediate steps finally together results in

$$\frac{\partial \frac{1}{2}\rho \mathbf{v} \cdot \mathbf{v}^{\text{T}}}{\partial t} = -\text{div}\ \left(\frac{1}{2}\rho(\mathbf{v} \cdot \mathbf{v}^{\text{T}})\, \mathbf{v} + \boldsymbol{\sigma}_{\text{M}} \cdot \mathbf{v}\right) + \boldsymbol{\sigma}_{\text{M}} \bullet \boldsymbol{\nabla} \mathbf{v} - \mathbf{r}_{p_{\text{EM}}} \cdot \mathbf{v}^{\text{T}}.$$

The **balance equation of kinetic energy** is thus

$$\frac{\partial\, e_{\mathrm{M}}}{\partial\, t} = -\mathrm{div}\,\left(e_{\mathrm{M}}\mathbf{v} + \widetilde{\mathbf{j}}_{e_{\mathrm{M}}}\right) + \widetilde{r}_{e_{\mathrm{M}}} \tag{2.180}$$

with the (diffusional) kinetic energy flux

$$\widetilde{\mathbf{j}}_{e_{\mathrm{M}}} = \boldsymbol{\sigma}_{\mathrm{M}} \cdot \mathbf{v} \tag{2.181}$$

and the kinetic energy density source

$$\widetilde{r}_{e_{\mathrm{M}}} = \boldsymbol{\sigma}_{\mathrm{M}} \bullet \boldsymbol{\nabla}\mathbf{v} + \varepsilon_0^{-1} n^{\mathrm{Q}} \mathbf{v} \cdot \mathbf{D}^{\mathrm{T}} + \mathbf{j}^{\mathrm{Q}} \cdot (\mathbf{B} \times \mathbf{v})^{\mathrm{T}}. \tag{2.182}$$

However, in accordance to the decomposition (2.137) and the following auxiliary calculation, one could rewrite the balance equation as

$$\frac{\partial\, e_{\mathrm{M}}}{\partial\, t} = -\mathrm{div}\,\left(e_{\mathrm{M}}\mathbf{v} + \mathbf{j}_{e_{\mathrm{M}}}\right) + r_{e_{\mathrm{M}}} \tag{2.183}$$

with

$$\mathbf{j}_{e_{\mathrm{M}}} = \boldsymbol{\sigma} \cdot \mathbf{v}^{\mathrm{T}} = (\boldsymbol{\sigma}_{\mathrm{M}} - \boldsymbol{\tau}_{\Delta}) \cdot \mathbf{v}^{\mathrm{T}} \tag{2.184}$$

$$r_{e_{\mathrm{M}}} = \boldsymbol{\sigma} \bullet \boldsymbol{\nabla}\mathbf{v} + \varepsilon_0^{-1} n^{\mathrm{F}} \mathbf{v} \cdot \mathbf{D}^{\mathrm{T}} + \mathbf{j}^{\mathrm{F}} \cdot (\mathbf{B} \times \mathbf{v})^{\mathrm{T}} + \mathbf{g}_{\mathrm{PM}} \cdot \mathbf{v}^{\mathrm{T}}. \tag{2.185}$$

Auxiliary calculation 2.22:

$$\begin{aligned} -\mathbf{r}_{p_{\mathrm{EM}}} \cdot \mathbf{v}^{\mathrm{T}} &= n^{\mathrm{F}}\, \varepsilon_0^{-1} \mathbf{D} \cdot \mathbf{v}^{\mathrm{T}} + \mathbf{j}^{\mathrm{F}} \cdot (\mathbf{B} \times \mathbf{v})^{\mathrm{T}} - (\mathrm{Div}\, \boldsymbol{\tau}_{\Delta}) \cdot \mathbf{v}^{\mathrm{T}} + \mathbf{g}_{\mathrm{PM}} \cdot \mathbf{v}^{\mathrm{T}} \\ &= \mathrm{div}\,(\boldsymbol{\tau}_{\Delta} \cdot \mathbf{v}^{\mathrm{T}}) + n^{\mathrm{F}} \varepsilon_0^{-1} \mathbf{D} \cdot \mathbf{v}^{\mathrm{T}} + \mathbf{j}^{\mathrm{F}} \cdot (\mathbf{B} \times \mathbf{v})^{\mathrm{T}} + \boldsymbol{\tau}_{\Delta} \bullet \boldsymbol{\nabla}\mathbf{v} + \mathbf{g}_{\mathrm{PM}} \cdot \mathbf{v}^{\mathrm{T}} \end{aligned}$$

Obviously, kinetic energy is not in general conserved, and the question arises *what* energy (density) is actually conserved. Summing the balance equations of kinetic (eq. 2.180) and EM-field (eq. 2.151) energy leads to

$$\begin{aligned} \frac{\partial\,(e_{\mathrm{M}} + e_{\mathrm{EM}} + \varepsilon_0^{-1}\mathbf{D} \cdot \mathbf{P})}{\partial\, t} = &-\mathrm{div}\,\left(e_{\mathrm{M}}\mathbf{v} + \mathbf{j}_{e_{\mathrm{M}}} + \mathbf{S}_{\mathrm{PM}}\right)) \\ &+ \boldsymbol{\sigma} \bullet \boldsymbol{\nabla}\mathbf{v} - \mathbf{j}^{\mathrm{F}} \cdot (\varepsilon_0^{-1}\mathbf{D} + \mathbf{B} \times \mathbf{v})^{\mathrm{T}} + \mathbf{g}_{\mathrm{PM}} \cdot \mathbf{v}^{\mathrm{T}} \\ &+ \left(\frac{\partial\, \mathbf{D}}{\partial\, t} + \frac{\partial\, \mathbf{B}}{\partial\, t} \times \mathbf{v}\right) \cdot \mathbf{P}^{\mathrm{T}} + \frac{\partial\, \mathbf{B}}{\partial\, t} \cdot \mathbf{M}^{\mathrm{T}}, \end{aligned} \tag{2.186}$$

which is also **not** a conservation equation. However, this is expectably, since *everyone* knows from experience that an electric current generates *heat*, or in other words, internal energy. This concept is stated rigorously in the following assumption.

Assumption 10 (First law of thermodynamics - conservation of energy)**.**

It is assumed that a unique energy density e_{I}, called **internal energy**, exists such that the **total energy density**

$$e = e_{\mathrm{I}} + e_{\mathrm{M}} + e_{\mathrm{PM}} \tag{2.187}$$

is conserved, *i.e.*

$$\int_{\omega} \frac{\partial e}{\partial t} + \operatorname{div}\left((e - e_{\mathrm{PM}})\mathbf{v} + \mathbf{j}_e\right) dV = 0 \qquad \forall \omega \in \Omega.^{7} \tag{2.188}$$

In vacuum the internal energy is supposed to vanish, *i.e.*

$$e_{\mathrm{I}}|_{\rho=0} = 0. \tag{2.190}$$

Thus the decomposition

$$e_{\mathrm{I}} = \rho\, u, \tag{2.191}$$

is motivated, and u is called **internal energy density**.

Next, the derivation of the internal energy balance is desired. From the implicit definition of the internal energy ($\rho\, u = e - e_{\mathrm{M}} - e_{\mathrm{PM}}$) it is clear that $\rho\, u$ obeys a general balance equation

$$\frac{\partial \rho\, u}{\partial t} = -\operatorname{div}\,(\rho\, u + \mathbf{j}_u) + r_u. \tag{2.192}$$

Similar to the force density $\mathbf{f}$ which arose in the derivation of the momentum balance, the explicit representation of the internal energy flux and source are now calculated. Subtracting eq. (2.186) from the total energy balance (2.188) leads to

$$\begin{aligned}\frac{\partial \rho\, u}{\partial t} = &-\operatorname{div}\,(\rho\, u\mathbf{v} + \mathbf{j}_e - \mathbf{j}_{e_{\mathrm{M}}} - \mathbf{S}_{\mathrm{PM}}) \\ &- \boldsymbol{\sigma} \bullet \boldsymbol{\nabla}\mathbf{v} + \mathbf{j}^{\mathrm{F}} \cdot \mathbf{E}^{\mathrm{T}} - \mathbf{g}_{\mathrm{PM}} \cdot \mathbf{v}^{\mathrm{T}} \\ &- \left(\frac{\partial \mathbf{D}}{\partial t} - \frac{\partial \mathbf{B}}{\partial t} \times \mathbf{v}\right) \cdot \mathbf{P}^{\mathrm{T}} - \frac{\partial \mathbf{B}}{\partial t} \cdot \mathbf{M}^{\mathrm{T}},\end{aligned} \tag{2.193}$$

which identifies the (diffusional) flux of the internal energy density (sometimes also called heat flux),

$$\mathbf{j}_u = \mathbf{j}_e - \mathbf{j}_{e_{\mathrm{M}}} - \mathbf{S}_{\mathrm{PM}} \tag{2.194}$$

and the **source of internal energy**

$$\begin{aligned} r_u = &-\boldsymbol{\sigma} \bullet \boldsymbol{\nabla}\mathbf{v} + \mathbf{j}^{\mathrm{F}} \cdot (\varepsilon_0^{-1}\mathbf{D} + \mathbf{B} \times \mathbf{v})^{\mathrm{T}} \\ &- \mathbf{g}_{\mathrm{PM}} \cdot \mathbf{v}^{\mathrm{T}} - \left(\frac{\partial \mathbf{D}}{\partial t} - \frac{\partial \mathbf{B}}{\partial t} \times \mathbf{v}\right) \cdot \mathbf{P}^{\mathrm{T}} - \frac{\partial \mathbf{B}}{\partial t} \cdot \mathbf{M}^{\mathrm{T}}.\end{aligned}$$

Corollary 6 (Internal energy balance on singular surfaces)**.**

The singular surface $\Sigma \in \Omega$ may also *cover* some internal energy, *e.g.* due to surface currents or reactions. Let thus $\underset{\mathrm{s}}{u}$ be the surface internal energy density (implicitly defined

[7] This decomposition might look somewhat arbitrary, however, it can be seen from the following *Gedankenexperiment*. In vacuum all mass densities vanish ($\rho_\alpha = 0,\ \alpha = 1, \ldots, n$) and thus also the free charge density n^{F} and the free current $\mathbf{j}^{\mathrm{F}}$. The total energy reduces to EM-field energy ($e = e_{\mathrm{PM}}$) and thus

$$\frac{\partial e}{\partial t} = -\operatorname{div}\,(e\,\mathbf{v} + \mathbf{S}_{\mathrm{PM}} - e_{\mathrm{PM}}) = -\operatorname{div}\,\mathbf{S}_{\mathrm{PM}} = \frac{\partial e_{\mathrm{PM}}}{\partial t}. \tag{2.189}$$

via a corresponding total energy) which fulfills some jump balance equation

$$\frac{\partial \underset{\mathrm{s}}{u}}{\partial t} = -\underset{\mathrm{s}}{\operatorname{div}}\,(\underset{\mathrm{s}}{u}\mathbf{v} + \underset{\mathrm{s}}{\mathbf{j}_u}) + \kappa \underset{\mathrm{s}}{u}\, v_n + \underset{\mathrm{s}}{r_u} + [\![\rho u \mathbf{v} + \mathbf{j}_u]\!] \cdot \mathbf{n}^{\mathrm{T}} \qquad \mathbf{x} \in \Sigma. \tag{2.195}$$

Without further derivation, I will state an internal energy source on the surface

$$\underset{\mathrm{s}}{r_u} = -\underset{\mathrm{s}}{p}\, \underset{\mathrm{s}}{\boldsymbol{\nabla}}\, \underset{\mathrm{s}}{\mathbf{v}} + \varepsilon_0^{-1} \underset{\mathrm{s}}{\mathbf{j}^{\mathrm{F}}} \cdot \underset{\mathrm{s}}{\mathbf{E}}^{\mathrm{T}}, \tag{2.196}$$

where

- $\underset{\mathrm{s}}{p}$ is the surface tension (and thus no viscous contributions are considered),
- $\underset{\mathrm{s}}{\mathbf{j}^{\mathrm{F}}}$ is a current due to free charges on the surface
- and $\underset{\mathrm{s}}{\mathbf{E}}$ the tangential component of $\mathbf{E}$ on Σ.

Of course, this could rigorously be derived from the jump conditions for momentum and total energy.

2.5 Summary on conservation of mass, momentum and energy

At this point, a brief summary on the above derivation is quite illustrative.

The continuum hypothesis was used to introduce mass densities ρ_α from some global mass M_α. With the introduction of (diffusional) mass fluxes $\mathbf{j}_\alpha$ and reaction rates r_α, the balance equations for each mass density where obtained,

$$\frac{\partial \rho_\alpha}{\partial t} = -\operatorname{div}\,(\rho_\alpha\, \mathbf{v} + \mathbf{j}_\alpha) + r_\alpha \qquad \alpha = 1, \ldots, \mathrm{n}. \tag{2.197}$$

Conservation of mass (and charge) was then deduced by assumption 4 (conservation of mass and charge in chemical reactions) as

$$\frac{\partial \rho}{\partial t} = -\operatorname{div}\,(\rho \mathbf{v} + \mathbf{j}) \tag{2.198}$$

$$\mathbf{j} = \sum_{\alpha=1}^{\mathrm{n}} \mathbf{j}_\alpha. \tag{2.199}$$

If the coordinate system is chosen such that $\mathbf{j} = 0$, then the Eulerian description is called standard coordinate system and the velocity field $\mathbf{v}$ is called barycentric velocity.

Based on general balance equations the electromagnetic field theory was then derived. The free charge density and current are related to mass densities and fluxes via

$$n^{\mathrm{F}} = e_0 \sum_{\alpha=1}^{\mathrm{n}} \frac{z_\alpha}{m_\alpha} \rho_\alpha \tag{2.200}$$

$$\mathbf{j}^{\mathrm{F}} = e_0 \sum_{\alpha=1}^{\mathrm{n}} \frac{z_\alpha}{m_\alpha} \mathbf{j}_\alpha, \tag{2.201}$$

which arise in the (macroscopic) Maxwell equations

$$\nabla \cdot (\mathbf{D} + \mathbf{P}) = n^{\mathrm{F}} \tag{2.202}$$

$$\nabla \cdot \mathbf{B} = 0 \tag{2.203}$$

$$\frac{\partial\,(\mathbf{D} + \mathbf{P})}{\partial\,t} = \mathrm{curl}\,(\frac{1}{\mu_0}\mathbf{B} - \mathbf{M} - \mathbf{P} \times \mathbf{v}) - \mathbf{i}^{\mathrm{F}} \tag{2.204}$$

$$\frac{\partial\,\mathbf{B}}{\partial\,t} = -\mathrm{curl}\,(\varepsilon_0^{-1}\mathbf{D}). \tag{2.205}$$

These where then exploited to derive a momentum and energy balance of the electromagnetic field, including polarization and magnetization. It was shown that neither momentum nor the energy of the EM-field is conserved, if free charges and currents are present.

Next, the momentum and (kinetic) energy balance of matter was derived, based on the continuum hypothesis of the corresponding macroscopic properties. Conservation of the total momentum led to the conclusion that the force density acting within the material is the Lorentz force, in addition to forces arising from polarization and magnetization. Newtons second (local) law was thus derived as

$$\frac{\partial \rho \mathbf{v}}{\partial t} = -\mathrm{Div}\ (\rho \mathbf{v} \otimes \mathbf{v} + \boldsymbol{\sigma}_{\mathrm{M}}) + n^{\mathrm{Q}}\,\varepsilon_0^{-1}\mathbf{D} - \mathbf{j}^{\mathrm{Q}} \times \mathbf{B} \tag{2.206}$$

and rewritten as

$$\frac{\partial \rho \mathbf{v}}{\partial t} = -\mathrm{Div}\ (\rho \mathbf{v} \otimes \mathbf{v} + \boldsymbol{\sigma}) + n^{\mathrm{F}}\,\varepsilon_0^{-1}\mathbf{D} - \mathbf{j}^{\mathrm{F}} \times \mathbf{B} + \mathbf{g}_{\mathrm{PM}}. \tag{2.207}$$

Essentially, in *linear materials* ($\mathbf{P} = \chi^P\mathbf{E},\ \mathbf{M} = \mu_0^{-1}\chi^M\mathbf{B}$) $\mathbf{g}_{\mathrm{PM}}$ will vanish. However, the momentum balance is the central equation to determine the velocity field $\mathbf{v}$ (general Navier–Stokes-equation). In mechanical equilibrium, however, it is the necessary restriction between mechanical stress σ (or later on pressure) and the electromagnetic force $\mathbf{f}$.

Based on a first law of thermodynamics, an internal energy density $\rho\,u$ was introduced, which covers all energy contributions that are neither due to kinetic energy nor due to EM-field energy. It was shown that the internal energy obeys the balance equation

$$\begin{aligned}\frac{\partial\,\rho u}{\partial\,t} &= -\mathrm{div}\ (\rho\,u + \mathbf{j}_u) - \boldsymbol{\sigma} \bullet \boldsymbol{\nabla}\mathbf{v} + \mathbf{j}^{\mathrm{F}} \cdot \mathbf{E} + \mathbf{g}_{\mathrm{PM}} \cdot \mathbf{v}^{\mathrm{T}} \\ &\quad - \left(\frac{\partial\,\mathbf{D}}{\partial\,t} - \frac{\partial\,\mathbf{B}}{\partial\,t} \times \mathbf{v}\right) \cdot \mathbf{P}^{\mathrm{T}} - \frac{\partial\,\mathbf{B}}{\partial\,t} \cdot \mathbf{M}^{\mathrm{T}}.\end{aligned} \tag{2.208}$$

Any medium or physical object will thus be described with the following (n + 4) (independent) variables and the corresponding (n + 4) balance equations, *i.e.*

- the n mass densities $\rho_\alpha(\mathbf{x}, t)$ obeying their respective mass balance (2.197)
- the barycentric[8] velocity $\mathbf{v}$ which is computed via the momentum balance (2.207)
- the electric field $\mathbf{E}$ and magnetic flux density $\mathbf{B}$ with respect to equations (2.202) - (2.205)
- and the internal energy density $\rho\,u$, computed with energy balance equation (2.208).

[8] Of course, any other material velocity could also be chosen. However, it was shown above that the momentum equation has the *simple* shape (2.207)only if the coordinate system is chosen such that $\mathbf{v}$ is the barycentric velocity.

However, the balance equations are yet underdetermined since

- the mass fluxes $\mathbf{j}_\alpha,\ \alpha = 1, \ldots, n-1$,
- the (material) stress tensor $\boldsymbol{\sigma}$,
- polarization $\mathbf{P}$ and magnetization $\mathbf{M}$,
- and the internal energy flux $\mathbf{j}_u$

are not known.

To **close the system of equations**, constitutive relationships or material functions are required, *e.g.*

$$\mathbf{j}_\alpha \propto \nabla \mu_\alpha(\rho_1, \ldots, \rho_\mathrm{n}, \mathbf{v}, \mathbf{E}, \mathbf{B}). \tag{2.209}$$

This access is now given with the introduction of an entropy density.

2.6 Entropy and the local second law

Entropy is the central concept in thermodynamics to couple mass or particles and internal energy. I will not derive the concept of entropy from statistical mechanics, but rather assume that there exits a function (or functional) which is called entropy and relates the extensive properties.

Classically in homogenous thermodynamics, the entropy function of the whole material is

$$S = S(U, \{N_\alpha\}_\alpha, V), \tag{2.210}$$

where U is the internal energy of the system, N_α the respective amount of species and V the (total) volume. However, in a field theoretical sense the number of variables decreases by one since the volume is implicitly incorporated in the density formulation of each extensive property.

Assumption 11 (Entropy density and flux)**.**

It is assumed that the entropy S of a physical object $\Omega \cup \Sigma$ could uniquely be written as[9]

$$S = \int_\Omega \rho(\mathbf{x}, t) \cdot s(\mathbf{x}, t)\, dV + \int_\Sigma \underset{\mathrm{s}}{s}(\mathbf{x}, t)\, dA \tag{2.211}$$

with a volumetric entropy density ρs and

$$\rho s = \mathfrak{s}(\rho u, \rho_1, \ldots, \rho_\mathrm{n}, \mathbf{P}, \mathbf{M}), \tag{2.212}$$

and the surface entropy density $\underset{\mathrm{s}}{s}$[10] with its representation

$$\underset{\mathrm{s}}{s} = \underset{\mathrm{s}}{\mathfrak{s}}(\underset{\mathrm{s}}{u}, \underset{\mathrm{s}}{\rho_1}, \ldots, \underset{\mathrm{s}}{\rho_\mathrm{n}}). \tag{2.213}$$

[9] The decomposition in ρs is quite convenient and again motivation from the fact that the entropy of vacuum vanishes. However, entropy contributions due to polarization are not necessarily bounded on a mass density.

[10] The surface entropy is not neccessarily proportional to a surface mass density, *e.g.* on phase boundaries[7].

The explicit representations $\mathfrak{s}(\rho u, \rho_1, \ldots, \rho_\mathrm{n}, \mathbf{P}, \mathbf{M})$ and $\underset{\mathrm{s}}{\mathfrak{s}}(\underset{\mathrm{s}}{u}, \underset{\mathrm{s}}{\rho_1}, \ldots, \underset{\mathrm{s}}{\rho_\mathrm{n}})$ are called (elementary)[11] **entropy functions**.
Further, the entropy is supposed to obey the global balance equation

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -\oint_{\partial\Omega} \mathbf{j}_s^\mathrm{T} \cdot d\mathbf{A} + \int_\Omega r_s \, dV - \oint_{\partial\Sigma} \underset{\mathrm{s}}{\mathbf{j}_s^\mathrm{T}} \cdot d\mathbf{s} + \int_\Sigma \underset{\mathrm{s}}{r_s} \, dV \tag{2.214}$$

and the continuum hypothesis.

Of course, the introduction of an entropy function $\mathfrak{s}(\rho u, \rho_1, \ldots, \rho_\mathrm{n}, \mathbf{P}, \mathbf{M})$ seems somehow arbitrary, except the number of variables. However, it is possible to derive this dependency via Lagrange multipliers, which was shown by J. Meixner, I. Müller and others [5, 22–26]. In this context an entropy function is defined without any known dependency on physical properties, and all balance equations (*i.e.* mass densities and internal energy) are added to the entropy balance with some Lagrange multipliers. The method is constructive, in the sense that it explains the (differential) relationship between entropy, internal energy and mass density (known as temperature and chemical potential) in the context of polarizable or magnetizable systems. However, I will not introduce thermodynamic potentials via Lagrange multipliers, but define them in their classical sense, extended to field properties.

Topic of the next sections is the derivation of the entropy balance equation

$$\frac{\partial \rho s}{\partial t} + \nabla \cdot (\rho s \mathbf{v} + \mathbf{j}_s) = r_s \tag{2.215}$$

and the jump conditions on the singular surface Σ. A (local) second law of thermodynamics is then assumed, stating $r_s \geq 0$ (as well as $\underset{\mathrm{s}}{r_s} \geq 0$). The exploitation of this constraint is called entropy principle and leads to several well know equations and restrictions, such as

- the Gibbs–Duhem equation
- the definition of the diffusional entropy flux
- the flux force relationships
- and the Onsager reciprocal principle.

For the sake of simplicity, I will first discuss the entropy principle for a non-polarize- and non-magnetizeable system, *i.e.* $\mathbf{P} = \mathbf{0}$, $\mathbf{M} = \mathbf{0}$ and $\rho s = \mathfrak{s}(\rho u, \rho_1, \ldots, \rho_\mathrm{n})$.

[11] The term "elementary" is used here, since later on variable changes and transformations will be applied to derive entropy functions which depend on the variable set $(T, \rho_1, \ldots, \rho_\mathrm{n})$ or $(T, p, c_1, \ldots, c_{n-1})$

2.6.1 Volumetric entropy balance without polarization and magnetization

To derive the entropy balance, one exploits the explicit dependency of the entropy function,

$$\frac{\partial \rho s}{\partial t} = \frac{\partial \mathfrak{s}(\rho u, \rho_1, \ldots, \rho_{\mathrm{n}}, \mathbf{E}, \mathbf{B})}{\partial t} = \frac{\partial \mathfrak{s}}{\partial \rho u} \cdot \frac{\partial \rho u}{\partial t} + \sum_{\alpha=1}^{\mathrm{n}} \frac{\partial \mathfrak{s}}{\partial \rho_\alpha} \cdot \frac{\partial \rho_\alpha}{\partial t} \tag{2.216}$$

The derivatives of the entropy with respect to the to (extensive) densities are[10]

- the Temperature T with

$$\frac{\partial \mathfrak{s}}{\partial \rho u} =: \frac{1}{T} \tag{2.217}$$

- and the Chemical potential μ_α with

$$\frac{\partial \mathfrak{s}}{\partial \rho_\alpha} =: -\frac{\mu_\alpha}{T}, \tag{2.218}$$

which leads to the compact form

$$\frac{\partial \rho s}{\partial t} = \frac{1}{T} \cdot \frac{\partial \rho u}{\partial t} - \sum_{\alpha=1}^{\mathrm{n}} \frac{\mu_\alpha}{T} \cdot \frac{\partial \rho_\alpha}{\partial t}. \tag{2.219}$$

Note that T is actually a function (or functional), similar to $\mathfrak{s}$, *i.e.*

$$T = T(\rho u, \rho_1, \ldots, \rho_{\mathrm{n}}) \tag{2.220}$$

and thus **not** an independent variable (similar for all other partial derivatives).

Insertion of the balance equations (2.208) and (2.197) for the time derivatives leads to

$$\frac{\partial \mathfrak{s}}{\partial t} = -\frac{1}{T}\Big(\mathrm{div}\ (\rho\, u\mathbf{v} + \mathbf{j}_u) - \mathbf{j}^{\mathrm{F}} \cdot \mathbf{E}^{\mathrm{T}} + (p\mathbf{Id} + \boldsymbol{\pi}) \bullet \boldsymbol{\nabla}\mathbf{v}\Big) \tag{2.221}$$

$$+ \sum_{\alpha=1}^{\mathrm{n}} \frac{\mu_\alpha}{T} \left(\mathrm{div}\,(\rho_\alpha\, \mathbf{v} + \mathbf{j}_\alpha) - r_\alpha\right) \tag{2.222}$$

where the decomposition $\boldsymbol{\sigma} = p\mathbf{Id} + \boldsymbol{\pi}$ (*c.f.* definition 9) was used.

The following auxiliary calculations are helpful in the further derivation.

Auxiliary calculation 2.23:

$$\frac{1}{T}\mathrm{div}\,\mathbf{j}_u = \mathrm{div}\,\left(\frac{1}{T}\mathbf{j}_u\right) - \nabla\frac{1}{T} \cdot \mathbf{j}_u^{\mathrm{T}}$$

$$\frac{\mu_\alpha}{T}\mathrm{div}\,\mathbf{j}_\alpha = \mathrm{div}\,\left(\frac{\mu_\alpha}{T}\mathbf{j}_\alpha\right) - \nabla\frac{\mu_\alpha}{T} \cdot \mathbf{j}_\alpha^{\mathrm{T}}$$

Auxiliary calculation 2.24:

$$\begin{aligned}
\operatorname{div}(\rho u\mathbf{v})\frac{1}{T} &= \operatorname{div}(\frac{1}{T}\rho u\mathbf{v}) - \rho u\left(\nabla\frac{1}{T}\right)\cdot\mathbf{v}\\
\operatorname{div}(\rho_\alpha\mathbf{v})\frac{\mu_\alpha}{T} &= \operatorname{div}(\frac{\mu_\alpha}{T}\rho_\alpha\mathbf{v}) - \rho_\alpha\left(\nabla\frac{\mu_\alpha}{T}\right)\cdot\mathbf{v}\\
\frac{1}{T}p\mathbf{Id}\bullet\boldsymbol{\nabla}\mathbf{v} &= \operatorname{div}(\frac{1}{T}p\,\mathbf{Id}\cdot\mathbf{v}) - \operatorname{Div}(\frac{1}{T}p\mathbf{Id})\cdot\mathbf{v} = \operatorname{div}(\frac{p}{T}\mathbf{v}) - \nabla\frac{p}{T}\cdot\mathbf{v}
\end{aligned}$$

Auxiliary calculation 2.25:

$$\begin{aligned}
\frac{\partial\mathfrak{s}}{\partial t} &= -\frac{1}{T}\left(\operatorname{div}(\rho\,u\mathbf{v}+\mathbf{j}_u) - \mathbf{j}^{\mathrm{F}}\cdot\mathbf{E}^{\mathrm{T}} + (p\,\mathbf{Id}+\boldsymbol{\pi})\bullet\boldsymbol{\nabla}\mathbf{v}\right)\\
&\quad + \sum_{\alpha=1}^{\mathrm{n}}\frac{\mu_\alpha}{T}\left(\operatorname{div}(\rho_\alpha\,\mathbf{v}+\mathbf{j}_\alpha) - r_\alpha\right)\\
&= -\operatorname{div}\left(\frac{1}{T}(\rho u - \sum_{\alpha=1}^{\mathrm{n}}\mu_\alpha\rho_\alpha + p)\,\mathbf{v} + \frac{1}{T}(\mathbf{j}_u - \sum_{\alpha=1}^{\mathrm{n}}\mu_\alpha\mathbf{j}_\alpha)\right)\\
&\quad + \left(\rho u\nabla\frac{1}{T} - \sum_{\alpha=1}^{\mathrm{n}}\rho_\alpha\nabla\frac{\mu_\alpha}{T} + \nabla\frac{p}{T}\right)\cdot\mathbf{v}^{\mathrm{T}}\\
&\quad + \mathbf{j}_u^{\mathrm{T}}\cdot\nabla\frac{1}{T} - \sum_{\alpha=1}^{\mathrm{n}}\mathbf{j}_\alpha^{\mathrm{T}}\cdot\left(\nabla\frac{\mu_\alpha}{T} - e_0\frac{1}{T}\frac{z_\alpha}{m_\alpha}\mathbf{E}\right) - \sum_{\alpha=1}^{\mathrm{n}}\frac{\mu_\alpha}{T}r_\alpha - \frac{1}{T}\boldsymbol{\pi}\bullet\boldsymbol{\nabla}\mathbf{v}
\end{aligned}$$

Thus one obtains the explicit representation

$$\begin{aligned}
\frac{\partial\mathfrak{s}}{\partial t} &= -\operatorname{div}\left(\frac{1}{T}(\rho u - \sum_{\alpha=1}^{\mathrm{n}}\mu_\alpha\rho_\alpha + p)\,\mathbf{v} + \frac{1}{T}(\mathbf{j}_u - \sum_{\alpha=1}^{\mathrm{n}}\mu_\alpha\mathbf{j}_\alpha)\right)\\
&\quad + \left(\rho u\nabla\frac{1}{T} - \sum_{\alpha=1}^{\mathrm{n}}\rho_\alpha\nabla\frac{\mu_\alpha}{T} + \nabla\frac{p}{T}\right)\cdot\mathbf{v}\\
&\quad + \mathbf{j}_u^{\mathrm{T}}\cdot\nabla\frac{1}{T} - \sum_{\alpha=1}^{\mathrm{n}}\mathbf{j}_\alpha^{\mathrm{T}}\cdot\left(\nabla\frac{\mu_\alpha}{T} - e_0\frac{1}{T}\frac{z_\alpha}{m_\alpha}\mathbf{E}\right) - \sum_{\alpha=1}^{\mathrm{n}}\frac{\mu_\alpha}{T}r_\alpha - \frac{1}{T}\boldsymbol{\pi}\bullet\boldsymbol{\nabla}\mathbf{v}. \qquad (2.223)
\end{aligned}$$

Since it assumed that there exits balance representation of the entropy, *i.e.*

$$\frac{\partial\,\rho s}{\partial\,t} = -\operatorname{div}(\rho s + \mathbf{j}_s) + r_s \qquad (2.224)$$

one concludes with a comparison principle between eq. (2.223) and eq. (2.224)

- the entropy density representation

$$\frac{1}{T}(\rho u - \sum_{\alpha=1}^{\mathrm{n}}\mu_\alpha\rho_\alpha + p) \stackrel{!}{=} \rho s,$$

- the entropy flux representation

$$\frac{1}{T}(\mathbf{j}_u - \sum_{\alpha=1}^{\mathrm{n}}\mu_\alpha\mathbf{j}_\alpha) \stackrel{!}{=} \mathbf{j}_s,$$

- the necessary condition

$$\left(\rho u \nabla \frac{1}{T} - \sum_{\alpha=1}^{\mathrm{n}} \rho_\alpha \nabla \frac{\mu_\alpha}{T} + \nabla \frac{p}{T}\right) \cdot \mathbf{v} \stackrel{!}{=} 0 \tag{2.225}$$

- and the entropy production

$$r_s \stackrel{!}{=} \mathbf{j}_u^{\mathrm{T}} \cdot \nabla \frac{1}{T} - \sum_{\alpha=1}^{\mathrm{n}} \mathbf{j}_\alpha^{\mathrm{T}} \cdot \left(\nabla \frac{\mu_\alpha}{T} - \frac{e_0 z_\alpha}{T\, m_\alpha} \mathbf{E}\right) - \sum_{\alpha=1}^{\mathrm{n}} \frac{\mu_\alpha}{T} r_\alpha - \boldsymbol{\pi} \bullet \boldsymbol{\nabla} \mathbf{v}. \tag{2.226}$$

This concept is called **entropy principle**.

Remark 7 (Gibbs- and Gibbs–Duhem-equation).

The explicit entropy representation

$$\frac{1}{T}(\rho u - \sum_{\alpha=1}^{\mathrm{n}} \mu_\alpha \rho_\alpha + p) = \rho s, \tag{2.227}$$

which is independent of the choice of variables and the actual coordinate system, is called **Gibbs-equation**[12]. Note that this equation determines the pressure p if the variables $(\rho u, \rho_1, \ldots, \rho_{\mathrm{n}})$ are known. The condition (2.225) should hold for every $\mathbf{v}$ and thus

$$\rho u \nabla \frac{1}{T} - \sum_{\alpha=1}^{\mathrm{n}} \rho_\alpha \nabla \frac{\mu_\alpha}{T} + \nabla \frac{p}{T} = \mathbf{0} \tag{2.228}$$

$$\stackrel{\mathrm{AC}(2.26)}{\Leftrightarrow} \quad \rho s \nabla T + \sum_{\alpha=1}^{\mathrm{n}} \rho_\alpha \nabla \mu_\alpha = \nabla p, \tag{2.229}$$

which is further called **Gibbs–Duhem-equation**.

Auxiliary calculation 2.26:

$$\begin{aligned}
&\rho u \nabla \frac{1}{T} - \sum_{\alpha=1}^{\mathrm{n}} \rho_\alpha \nabla \frac{\mu_\alpha}{T} + \nabla \frac{p}{T} \\
=&(\rho u - \sum_{\alpha=1}^{\mathrm{n}} \mu_\alpha \rho_\alpha + p) \nabla \frac{1}{T} - \frac{1}{T} \sum_{\alpha=1}^{\mathrm{n}} \rho_\alpha \nabla \mu_\alpha + \frac{1}{T} \nabla p \\
=&-\frac{1}{T}\left(\frac{1}{T}(\rho u - \sum_{\alpha=1}^{\mathrm{n}} \mu_\alpha \rho_\alpha + p) \nabla T + \sum_{\alpha=1}^{\mathrm{n}} \rho_\alpha \nabla \mu_\alpha - \nabla p\right)
\end{aligned}$$

Thus, the explicit **entropy balance equation** (without polarization and magnetization)

$$\frac{\partial\, \rho s}{\partial\, t} = -\mathrm{div}\,(\rho s\, \mathbf{v} + \mathbf{j}_u) + r_s \tag{2.230}$$

is derived, and the second law of thermodynamics can be stated.

Assumption 12 (Second law of thermodynamics)**.**

[12] In classical thermodynamics as well as in some theories of non-equilibrium thermodynamics the Gibbs–Duhem equation is postulated, while here it is derived from general conservation equations.

It is assumed that the entropy production

$$R_S = \int_\Omega r_s \, dV \geq 0 \tag{2.231}$$

and that this relations holds **for every** $\omega \in \Omega$. Thus, the **local second law of thermodynamics**

$$r_s(\mathbf{x}, t) \geq 0 \qquad \forall (\mathbf{x}, t) \in \Omega \times I \tag{2.232}$$

is formulated.

2.6.2 Volumetric entropy principle with polarization and magnetization

The extension of the entropy principle to systems with polarization and magnetization is not straight forward, in the sense that different strategies are found in literature. While Liu and Müller [26, 27] again use Lagrange multiplies, the approach of de Groot, Jackson and others [10, 11, 15] is an extension of the comparison principle (eq. (2.223) and eq. (2.224)). I will somehow follow a compromise, using a comparison principle to deduce a *good candidate* for the resulting expressions $\frac{\partial \rho s}{\partial \mathbf{D}}$ and $\frac{\partial \rho s}{\partial \mathbf{B}}$, which is shown now.

From an entropy function $\mathfrak{s} = \mathfrak{s}(\rho u, \rho_1, \ldots, \rho_\mathrm{n}, \mathbf{E}, \mathbf{B})$ one obtains

$$\frac{\partial \mathfrak{s}}{\partial t} = \frac{1}{T} \cdot \frac{\partial \rho u}{\partial t} - \sum_{\alpha=1}^{\mathrm{n}} \frac{\mu_\alpha}{T} \cdot \frac{\partial \rho_\alpha}{\partial t} + \frac{\partial \mathfrak{s}}{\partial \varepsilon_0^{-1} \mathbf{D}} \cdot \frac{\partial \varepsilon_0^{-1} \mathbf{D}^\mathrm{T}}{\partial t} + \frac{\partial \mathfrak{s}}{\partial \mathbf{B}} \cdot \frac{\partial \mathbf{B}}{\partial t}. \tag{2.233}$$

Inserting again the balance equations (2.208) and (2.197), however, accounting for the internal energy contributions due to polarization and magnetization, one obtains

$$\begin{aligned}
\frac{\partial \mathfrak{s}}{\partial t} = & -\frac{1}{T} \mathrm{div}\, (\rho u \mathbf{v} + \mathbf{j}_u) + \frac{1}{T} \mathbf{j}^\mathrm{F} \cdot \mathbf{E}^\mathrm{T} \\
& - \frac{1}{T} ((p + \frac{1}{2} \varepsilon_0^{-1} \mathbf{D} \cdot \mathbf{P}^\mathrm{T} - \mathbf{B} \cdot \mathbf{M}^\mathrm{T}) \mathbf{Id} + \boldsymbol{\pi}) \bullet \boldsymbol{\nabla} \mathbf{v} \\
& + \frac{1}{T} \mathbf{P} \cdot \frac{\partial \mathbf{D}^\mathrm{T}}{\partial t} + \frac{\partial \mathfrak{s}}{\partial \varepsilon_0^{-1} \mathbf{D}} \cdot \frac{\partial \varepsilon_0^{-1} \mathbf{D}^\mathrm{T}}{\partial t} \\
& + \frac{1}{T} (\mathbf{M} + \mathbf{P} \times \mathbf{v}) \cdot \frac{\partial \mathbf{B}}{\partial t} + \frac{\partial \mathfrak{s}}{\partial \mathbf{B}} \cdot \frac{\partial \mathbf{B}}{\partial t} \\
& + \sum_{\alpha=1}^{\mathrm{n}} \frac{\mu_\alpha}{T} \left(\mathrm{div}\, (\rho_\alpha \mathbf{v} + \mathbf{j}_\alpha) - r_\alpha \right) + \frac{1}{T} \mathbf{g}_\mathrm{PM} \cdot \mathbf{v}^\mathrm{T}.
\end{aligned} \tag{2.234}$$

Applying again the entropy principle (*c.f.* page 85) one concludes

- the entropy density representation

$$\frac{1}{T} (\rho u - \sum_{\alpha=1}^{\mathrm{n}} \mu_\alpha \rho_\alpha + p + \frac{1}{2} \varepsilon_0^{-1} \mathbf{D} \cdot \mathbf{P}^\mathrm{T} - \frac{1}{2} \mathbf{B} \cdot \mathbf{M}^\mathrm{T}) \stackrel{!}{=} \rho s,$$

- the entropy flux representation

$$\frac{1}{T} (\mathbf{j}_u - \sum_{\alpha=1}^{\mathrm{n}} \mu_\alpha \mathbf{j}_\alpha) \stackrel{!}{=} \mathbf{j}_s, \tag{2.235}$$

- the necessary condition (for all $\mathbf{v}$)

$$\left(\rho u \nabla \frac{1}{T} - \sum_{\alpha=1}^{\mathrm{n}} \rho_\alpha \nabla \frac{\mu_\alpha}{T} + \nabla \left(\frac{p}{T} + \frac{1}{2}\varepsilon_0^{-1}\mathbf{D}\cdot\mathbf{P}^{\mathrm{T}} - \frac{1}{2}\mathbf{B}\cdot\mathbf{M}^{\mathrm{T}}\right) + \frac{1}{T}\mathbf{g}_{\mathrm{PM}}\right)\cdot\mathbf{v}^{\mathrm{T}} \stackrel{!}{=} 0,$$

- polarization

$$\frac{\partial\,\mathfrak{s}}{\partial\,\varepsilon_0^{-1}\,\mathbf{D}} = -\frac{\mathbf{P}}{T}, \tag{2.236}$$

- magnetization

$$\frac{\partial\,\mathfrak{s}}{\partial\,\mathbf{B}} = -\frac{\mathbf{M}+\mathbf{P}\times\mathbf{v}}{T}, \tag{2.237}$$

- and finally the entropy production

$$r_s \stackrel{!}{=} \nabla\frac{1}{T}\cdot\mathbf{j}_u^{\mathrm{T}} - \sum_{\alpha=1}^{\mathrm{n}}\mathbf{j}_\alpha\cdot\left(\nabla\frac{\mu_\alpha}{T} - \frac{e_0 z_\alpha}{T\,m_\alpha}\mathbf{E}\right) - \sum_{\alpha=1}^{\mathrm{n}}\frac{\mu_\alpha}{T}r_\alpha - \boldsymbol{\pi}\bullet\boldsymbol{\nabla}\mathbf{v}.$$

It is convenient to decompose the entropy production as

$$r_s = r_{s,\boldsymbol{\pi}} + r_{s,\mathbf{j}} + r_{s,r} \tag{2.238}$$

with

- the viscous entropy production

$$r_{s,\boldsymbol{\pi}} = -\boldsymbol{\pi}\bullet\boldsymbol{\nabla}\mathbf{v}, \tag{2.239}$$

- the flux entropy production

$$r_{s,\mathbf{j}} = \nabla\frac{1}{T}\cdot\mathbf{j}_u^{\mathrm{T}} - \sum_{\alpha=1}^{\mathrm{n}}\mathbf{j}_\alpha\cdot\left(\nabla\frac{\mu_\alpha}{T} - \frac{e_0 z_\alpha}{T\,m_\alpha}\mathbf{E}\right), \tag{2.240}$$

- and the reaction entropy production

$$r_{s,r} = -\sum_{\alpha=1}^{\mathrm{n}}\frac{\mu_\alpha}{T}r_\alpha. \tag{2.241}$$

Of course this concept has to be applied with care since the conclusions

$$\frac{\partial\,\rho s}{\partial\,\mathbf{E}} \stackrel{!}{=} -\frac{1}{T}\mathbf{P} \tag{2.242}$$

$$\frac{\partial\,\rho s}{\partial\,\mathbf{B}} \stackrel{!}{=} -\frac{1}{T}(\mathbf{M}+\mathbf{P}\times\mathbf{v}) \tag{2.243}$$

are only **necessary** conditions, in the sense that this **choice** does not violate the stated assumptions (mainly the local second law). However, it is a constructive method and sufficient for my purpose.

Lemma 3 (Gibbs and Gibbs–Duhem-equation for polarize- and magnetizeable material)**.**

The entropy representation

$$\rho u - \sum_{\alpha=1}^{\mathrm{n}} \mu_\alpha \rho_\alpha + p + \frac{1}{2}\varepsilon_0^{-1}\mathbf{D}\cdot\mathbf{P}^{\mathrm{T}} - \frac{1}{2}\mathbf{B}\cdot\mathbf{M}^{\mathrm{T}} = T\rho s \tag{2.244}$$

is called Gibbs-equation for PM-media and the relation

$$\rho u \nabla\frac{1}{T} - \sum_{\alpha=1}^{\mathrm{n}} \rho_\alpha \nabla\frac{\mu_\alpha}{T} + \nabla\left(\frac{p}{T} + \frac{1}{2}\varepsilon_0^{-1}\mathbf{D}\cdot\mathbf{P}^{\mathrm{T}} + \frac{1}{2}\mathbf{B}\cdot\mathbf{M}\right) + \frac{1}{T}\mathbf{g}_{\mathrm{PM}} = \mathbf{0} \tag{2.245}$$

generalized Gibbs–Duhem equation.

2.6.3 Entropy balance on singular surfaces

Since the entropy ρs obeys a balance equation in Ω, there also hold some jump conditions for a singular surface $\Sigma \in \Omega$. However, the surface itself could have entropy contributions, which was stated with the introduction of a surface entropy density $\underset{\mathrm{s}}{s}$. The corresponding balance equation (or jump condition) is

$$\frac{\partial \underset{\mathrm{s}}{s}}{\partial t} = -\underset{\mathrm{s}}{\operatorname{div}}\left(\underset{\mathrm{s}}{s}\mathbf{v} + \underset{\mathrm{s}}{\mathbf{j}_s}\right) - \kappa \underset{\mathrm{s}}{s}\cdot v_n + \underset{\mathrm{s}}{r_s} - [\![\rho s\mathbf{v} + \mathbf{j}_s]\!]\cdot\mathbf{n}^{\mathrm{T}}, \tag{2.246}$$

which is simply obtained from the global representation and the continuum hypothesis.

Again, the explicit representations of $\underset{\mathrm{s}}{\mathbf{j}_s}$ and $\underset{\mathrm{s}}{r_s}$ are desired. With the entropy function[13] $\underset{\mathrm{s}}{\mathfrak{s}}(\underset{\mathrm{s}}{u}, \underset{\mathrm{s}}{\rho_1}, \ldots, \underset{\mathrm{s}}{\rho_{\mathrm{n}}})$ one obtains

$$\frac{\partial \underset{\mathrm{s}}{\mathfrak{s}}}{\partial t} = \frac{\partial \underset{\mathrm{s}}{s}}{\partial \underset{\mathrm{s}}{u}}\cdot\frac{\partial \underset{\mathrm{s}}{u}}{\partial t} + \sum_{\alpha=1}^{\mathrm{n}} \frac{\partial \underset{\mathrm{s}}{s}}{\partial \underset{\mathrm{s}}{\rho_\alpha}}\cdot\frac{\partial \underset{\mathrm{s}}{\rho_\alpha}}{\partial t}. \tag{2.247}$$

Analogous to the volume, the surface temperature $\underset{\mathrm{s}}{T}$ and chemical potentials $\underset{\mathrm{s}}{\mu_\alpha}$ are introduced as

$$\frac{1}{\underset{\mathrm{s}}{T}} = \frac{\partial \underset{\mathrm{s}}{s}}{\partial \underset{\mathrm{s}}{u}} \tag{2.248}$$

$$-\frac{\underset{\mathrm{s}}{\mu_\alpha}}{\underset{\mathrm{s}}{T}} = \frac{\partial \underset{\mathrm{s}}{s}}{\partial \underset{\mathrm{s}}{\rho_\alpha}} \qquad \alpha = 1, \ldots, \mathrm{n}. \tag{2.249}$$

Inserting the balance equations (2.195), (2.196) and (2.12) leads to

$$\begin{aligned}\frac{\partial \underset{\mathrm{s}}{\mathfrak{s}}}{\partial t} = &-\frac{1}{T}\underset{\mathrm{s}}{\operatorname{div}}\left(\underset{\mathrm{s}}{u}\mathbf{v} + \underset{\mathrm{s}}{\mathbf{j}_u}\right) - \kappa\frac{1}{T}\left(\underset{\mathrm{s}}{u} - \sum_{\alpha=1}^{\mathrm{n}} \underset{\mathrm{s}}{\mu_\alpha}\cdot\underset{\mathrm{s}}{\rho_\alpha}\right)\cdot v_n + \sum_{\alpha=1}^{\mathrm{n}} \frac{\underset{\mathrm{s}}{\mu_\alpha}}{\underset{\mathrm{s}}{T}}\cdot\left(\underset{\mathrm{s}}{\operatorname{div}}\left(\underset{\mathrm{s}}{\rho_\alpha}\underset{\mathrm{s}}{\mathbf{v}} + \underset{\mathrm{s}}{\mathbf{j}_\alpha}\right) - \underset{\mathrm{s}}{r_\alpha}\right)\\ &- \frac{\underset{\mathrm{s}}{p}}{\underset{\mathrm{s}}{T}}\underset{\mathrm{s}}{\boldsymbol{\nabla}}\underset{\mathrm{s}}{\mathbf{v}} + \frac{1}{\underset{\mathrm{s}}{T}\cdot\varepsilon_0}\underset{\mathrm{s}}{\mathbf{j}^{\mathrm{F}}}\cdot\underset{\mathrm{s}}{\mathbf{E}} - \frac{1}{\underset{\mathrm{s}}{T}}[\![\rho u\mathbf{v} + \mathbf{j}_u]\!]\cdot\mathbf{n}^{\mathrm{T}} + \sum_{\alpha=1}^{\mathrm{n}} \frac{\underset{\mathrm{s}}{\mu_\alpha}}{\underset{\mathrm{s}}{T}}[\![\rho_\alpha\mathbf{v} + \mathbf{j}_\alpha]\!]\cdot\mathbf{n}^{\mathrm{T}}.\end{aligned} \tag{2.250}$$

Corollary 7 (Continuity of temperature)**.**

[13] For the sake of simplicity in the derivation, I neglect here polarization and magnetization.

The temperature T is assumed to be continuous across a singular surface, with limit value $\underset{\mathrm{s}}{T}$, *i.e.*

$$\lim_{h\to 0} T(\mathbf{x}+h\cdot\mathbf{n},t) = \lim_{h\to 0} T(\mathbf{x}-h\cdot\mathbf{n},t) = \underset{\mathrm{s}}{T}(\mathbf{x},t) \qquad \mathbf{x}\in\Sigma \tag{2.251}$$

The continuity of temperature and the auxiliary calculation 2.27 lead to

$$\begin{aligned}
\frac{\partial \underset{\mathrm{s}}{\mathfrak{s}}}{\partial t} = &-\underset{\mathrm{s}}{\operatorname{div}}\left(\frac{1}{\underset{\mathrm{s}}{T}}(\underset{\mathrm{s}}{u}-\sum_{\alpha=1}^{\mathrm{n}}\underset{\mathrm{s}}{\mu_\alpha}\underset{\mathrm{s}}{\rho_\alpha}+\underset{\mathrm{s}}{p})+\frac{1}{\underset{\mathrm{s}}{T}}(\underset{\mathrm{s}}{\mathbf{j}_u}-\sum_{\alpha=1}^{\mathrm{n}}\underset{\mathrm{s}}{\mu_\alpha}\underset{\mathrm{s}}{\mathbf{j}_\alpha})\right)\\
&+\left(\underset{\mathrm{s}}{u}\underset{\mathrm{s}}{\nabla}\frac{1}{\underset{\mathrm{s}}{T}}-\sum_{\alpha=1}^{\mathrm{n}}\underset{\mathrm{s}}{\rho_\alpha}\underset{\mathrm{s}}{\nabla}\frac{\underset{\mathrm{s}}{\mu_\alpha}}{\underset{\mathrm{s}}{T}}+\underset{\mathrm{s}}{\nabla}\frac{\underset{\mathrm{s}}{p}}{\underset{\mathrm{s}}{T}}\right)\cdot\underset{\mathrm{s}}{\mathbf{v}}\\
&+\underset{\mathrm{s}}{\mathbf{j}_u^{\mathrm{T}}}\cdot\underset{\mathrm{s}}{\nabla}\frac{1}{\underset{\mathrm{s}}{T}}-\sum_{\alpha=1}^{\mathrm{n}}\underset{\mathrm{s}}{\mathbf{j}_\alpha^{\mathrm{T}}}\cdot\left(\underset{\mathrm{s}}{\nabla}\frac{\underset{\mathrm{s}}{\mu_\alpha}}{\underset{\mathrm{s}}{T}}-\frac{e_0 z_\alpha}{\underset{\mathrm{s}}{T}\,m_\alpha\varepsilon_0}\underset{\mathrm{s}}{\mathbf{E}}\right)-\sum_{\alpha=1}^{\mathrm{n}}\frac{\underset{\mathrm{s}}{\mu_\alpha}}{T}\underset{\mathrm{s}}{r_\alpha}\\
&-\frac{1}{\underset{\mathrm{s}}{T}}\left(\kappa(\underset{\mathrm{s}}{u}-\sum_{\alpha=1}^{\mathrm{n}}\underset{\mathrm{s}}{\mu_\alpha}\cdot\underset{\mathrm{s}}{\rho_\alpha})-[\![p]\!]\right)\cdot v_n\\
&-[\![\rho s\mathbf{v}+\mathbf{j}_s]\!]\cdot\mathbf{n}^{\mathrm{T}}-[\![\sum_{\alpha=1}^{\mathrm{n}}\left(\frac{\mu_\alpha}{T}-\frac{\underset{\mathrm{s}}{\mu_\alpha}}{T}\right)(\rho_\alpha\mathbf{v}+\mathbf{j}_\alpha)]\!]\cdot\mathbf{n}^{\mathrm{T}}.
\end{aligned} \tag{2.252}$$

Auxiliary calculation 2.27:
With the entropy density and flux representations

$$\begin{aligned}
\frac{1}{T}(\rho u-\sum_{\alpha=1}^{\mathrm{n}}\mu_\alpha\rho_\alpha+p) &= \rho s\\
\frac{1}{T}(\mathbf{j}_u-\sum_{\alpha=1}^{\mathrm{n}}\mu_\alpha\mathbf{j}_\alpha) &= \mathbf{j}_s,
\end{aligned}$$

one obtains

$$\begin{aligned}
&-\frac{1}{\underset{\mathrm{s}}{T}}[\![\rho u\mathbf{v}+\mathbf{j}_u]\!]+\sum_{\alpha=1}^{\mathrm{n}}\frac{\underset{\mathrm{s}}{\mu_\alpha}}{\underset{\mathrm{s}}{T}}[\![\rho_\alpha\mathbf{v}+\mathbf{j}_\alpha]\!]\\
&=-[\![\rho s\mathbf{v}+\mathbf{j}_s]\!]+\frac{1}{\underset{\mathrm{s}}{T}}[\![p\mathbf{v}]\!]-[\![\sum_{\alpha=1}^{\mathrm{n}}\frac{\mu_\alpha}{T}(\rho_\alpha\mathbf{v}+\mathbf{j}_\alpha)]\!]+[\![\sum_{\alpha=1}^{\mathrm{n}}\frac{\underset{\mathrm{s}}{\mu_\alpha}}{T}(\rho_\alpha\mathbf{v}+\mathbf{j}_\alpha)]\!]\\
&=-[\![\rho s\mathbf{v}+\mathbf{j}_s]\!]+\frac{1}{\underset{\mathrm{s}}{T}}[\![p\mathbf{v}]\!]-[\![\sum_{\alpha=1}^{\mathrm{n}}\left(\frac{\mu_\alpha}{T}-\frac{\underset{\mathrm{s}}{\mu_\alpha}}{T}\right)(\rho_\alpha\mathbf{v}+\mathbf{j}_\alpha)]\!]
\end{aligned}$$

Of course, similar relations like the Gibbs and the Gibbs–Duhem equation are desired for the surface. A comparison of (2.252) with (2.246) leads to

- the surface Gibbs equation

$$\underset{\mathrm{s}}{T}\underset{\mathrm{s}}{s} = \underset{\mathrm{s}}{u}-\sum_{\alpha=1}^{\mathrm{n}}\underset{\mathrm{s}}{\mu_\alpha}\underset{\mathrm{s}}{\rho_\alpha}+\underset{\mathrm{s}}{p}, \tag{2.253}$$

- the surface Gibbs–Duhem equation

$$\underset{\mathrm{s}}{s}\,\underset{\mathrm{s}}{\nabla}\,\underset{\mathrm{s}}{T} + \sum_{\alpha=1}^{\mathrm{n}} \underset{\mathrm{s}}{\rho_\alpha}\,\underset{\mathrm{s}}{\nabla}\,\underset{\mathrm{s}}{T} = \underset{\mathrm{s}}{\nabla}\,\underset{\mathrm{s}}{p}, \tag{2.254}$$

- and the surface entropy flux representation

$$\frac{1}{\underset{\mathrm{s}}{T}}\left(\underset{\mathrm{s}}{\mathbf{j}_u} - \sum_{\alpha=1}^{\mathrm{n}} \underset{\mathrm{s}}{\mu_\alpha}\,\underset{\mathrm{s}}{\mathbf{j}_\alpha}\right) = \underset{\mathrm{s}}{\mathbf{j}_s}. \tag{2.255}$$

Next, the curvature and jump terms are investigated, which require the following assumption.

Assumption 13 (Young–Laplace equation)**.**

I will assume that on the singular surface Σ the surface tension is simply related to the pressure jump and the curvature via

$$-\kappa \cdot \underset{\mathrm{s}}{p} = [\![p]\!]. \tag{2.256}$$

This relation is also called **Young–Laplace equation**. Further, this relation implies

$$-\kappa \cdot \underset{\mathrm{s}}{p}\, v_n = [\![p]\!]\, v_n = [\![p\mathbf{v}]\!] \cdot \mathbf{n}^{\mathrm{T}} \tag{2.257}$$

since the jump occurs in normal direction of Σ, which itself is a material surface (*c.f.* page 1.1.2 *f.f.*)

With this derivations the curvature term in (2.252) is

$$\kappa(\underset{\mathrm{s}}{u} - \sum_{\alpha=1}^{\mathrm{n}} \underset{\mathrm{s}}{\mu_\alpha} \cdot \underset{\mathrm{s}}{\rho_\alpha}) - [\![p]\!] = \kappa\frac{1}{T}(\underset{\mathrm{s}}{u} - \sum_{\alpha=1}^{\mathrm{n}} \underset{\mathrm{s}}{\mu_\alpha} \cdot \underset{\mathrm{s}}{\rho_\alpha}) + \kappa \cdot \underset{\mathrm{s}}{p} = \kappa \underset{\mathrm{s}}{T}\underset{\mathrm{s}}{s} \tag{2.258}$$

and one thus one deduces (again by comparison to eq. (2.246)) the surface entropy production

$$\begin{aligned} \underset{\mathrm{s}}{r_s} = \underset{\mathrm{s}}{\mathbf{j}_u} \cdot \underset{\mathrm{s}}{\nabla}\frac{1}{\underset{\mathrm{s}}{T}} - \sum_{\alpha=1}^{\mathrm{n}} \underset{\mathrm{s}}{\mathbf{j}_\alpha} \cdot \left(\underset{\mathrm{s}}{\nabla}\frac{\underset{\mathrm{s}}{\mu_\alpha}}{\underset{\mathrm{s}}{T}} - \frac{e_0 z_\alpha}{\underset{\mathrm{s}}{T}\, m_\alpha \varepsilon_0}\underset{\mathrm{s}}{\mathbf{E}}\right) \\ - \sum_{\alpha=1}^{\mathrm{n}} \frac{\underset{\mathrm{s}}{\mu_\alpha}}{T}\underset{\mathrm{s}}{r_\alpha} - [\![\sum_{\alpha=1}^{\mathrm{n}} \left(\frac{\mu_\alpha}{T} - \frac{\underset{\mathrm{s}}{\mu_\alpha}}{T}\right)(\rho_\alpha \mathbf{v} + \mathbf{j}_\alpha)]\!] \end{aligned} \tag{2.259}$$

- with the surface reaction entropy production

$$\underset{\mathrm{s}}{r_{s,r}} = -\sum_{\alpha=1}^{\mathrm{n}} \frac{\underset{\mathrm{s}}{\mu_\alpha}}{T}\underset{\mathrm{s}}{r_\alpha} \tag{2.260}$$

- the surface flux entropy production

$$\underset{\mathrm{s}}{r_{s,\mathbf{j}}} = \underset{\mathrm{s}}{\mathbf{j}_u} \cdot \underset{\mathrm{s}}{\nabla}\frac{1}{\underset{\mathrm{s}}{T}} - \sum_{\alpha=1}^{\mathrm{n}} \underset{\mathrm{s}}{\mathbf{j}_\alpha} \cdot \left(\underset{\mathrm{s}}{\nabla}\frac{\underset{\mathrm{s}}{\mu_\alpha}}{\underset{\mathrm{s}}{T}} - \frac{e_0 z_\alpha}{\underset{\mathrm{s}}{T}\, m_\alpha \varepsilon_0}\underset{\mathrm{s}}{\mathbf{E}}\right). \tag{2.261}$$

- and the flux jump entropy production

$$\underset{\mathrm{s}}{r}_{s,[\![\mathbf{j}]\!]} - [\![\sum_{\alpha=1}^{\mathrm{n}} \left(\frac{\mu_\alpha}{T} - \frac{\underset{\mathrm{s}}{\mu_\alpha}}{T} \right) (\rho_\alpha \mathbf{v} + \mathbf{j}_\alpha)]\!]. \tag{2.262}$$

Corollary 8 (Continuity of the chemical potential at singular surfaces)**.**

Similar to the temperature T I assume throughout the rest of the work that the chemical potential is continuos across singular surfaces, *i.e.*

$$\lim_{h\to 0} \mu_\alpha(\mathbf{x} + h\mathbf{n}) = \lim_{h\to 0} \mu_\alpha(\mathbf{x} - h\mathbf{n}) = \underset{\mathrm{s}}{\mu_\alpha}(\mathbf{x}, t) \qquad \mathbf{x} \in \Sigma. \tag{2.263}$$

In consequence, the flux jump entropy production $\underset{\mathrm{s}}{r}_{s,[\![\mathbf{j}]\!]}$ vanishes.

Equivalent to the volume a local second law of thermodynamics is now stated.

Assumption 14 (Second law of thermodynamics for surfaces)**.**

It is assumed that the entropy production on the surface Σ

$$\underset{\mathrm{s}}{R}_S = \int_\Sigma \underset{\mathrm{s}}{r}_s \, dA \geq 0 \tag{2.264}$$

and that this relation hold **for every** $\sigma \in \Sigma$. This leads to

$$\underset{\mathrm{s}}{r}_s(\mathbf{x}, t) \geq 0 \qquad \forall (\mathbf{x}, t) \in \Sigma \times I \tag{2.265}$$

and is called **local surface second law of thermodynamics**.

2.7 Exploitation of the second law

The entropy principle led to explicit representations of the entropy balance equations, and consequently, to the entropy production rate r_s in Ω and $\underset{\mathrm{s}}{r}_s$ in Σ. The postulated non-negativity is now exploited to introduce conditions on the reaction rates as well as on flux.

It was shown that the entropy production could be written as a sum

$$r_s = r_{s,\boldsymbol{\pi}} + r_{s,\mathbf{j}} + r_{s,r}. \tag{2.266}$$

This partition is not randomly since each source term has a unique underlying structure, *i.e.*

- $r_{s,\boldsymbol{\pi}}$ consist of tensor scalar products
- $r_{s,\mathbf{j}}$ of vector scalar products
- and $r_{s,r}$ of simple products.

In the last century the question arose if this inherent structure ensures that each of the terms itself obeys a non-negativity restriction [25, 28–31], which is sometimes called Curie principle [10].

Assumption 15 (Curie principle)**.**
Throughout this work it is assumed that the entropy production r_s decomposes into

$$r_s = r_{s,\boldsymbol{\pi}} + r_{s,\mathbf{j}} + r_{s,r} \tag{2.267}$$

and that each production is non-negative, *i.e.*

$$r_{s,\boldsymbol{\pi}} \geq 0, \quad r_{s,\mathbf{j}} \geq 0 \quad \text{and} \quad r_{s,r} \geq 0.$$

The same is assumed to hold true for the surface entropy production $\underset{\mathrm{s}}{r}_s = \underset{\mathrm{s}}{r}_{s,r} + \underset{\mathrm{s}}{r}_{s,\mathbf{j}}$ with

$$\underset{\mathrm{s}}{r}_{s,r} \geq 0 \quad \text{and} \quad \underset{\mathrm{s}}{r}_{s,\mathbf{j}} \geq 0.$$

Curie's principle allows thus for an exploitation of the entropy principle on each term.

2.7.1 Affinity conditions

First, reconsider the entropy production due to chemical reactions, *i.e.*

$$r_{s,r} = -\sum_{\alpha=1}^{\mathrm{n}} \frac{1}{T}\mu_\alpha \cdot r_\alpha = -\sum_{k=1}^{\mathrm{n}_r} q_k \cdot \underbrace{\left(\frac{1}{T}\sum_{\alpha=1}^{\mathrm{n}} \nu_{\alpha,k} m_\alpha \mu_\alpha\right)}_{=:\lambda_k}. \tag{2.268}$$

The abbreviation λ_k is called **affinity** of reaction k. Due to the conservation of mass constraint one could also write (*without loss of generality*)

$$\lambda_k = \frac{1}{T}\sum_{\alpha=1}^{\mathrm{n}-1}(\nu_{\alpha,k} m_\alpha \mu_\alpha - \nu_{\mathrm{n},k} m_{\mathrm{n}} \mu_{\mathrm{n}}). \tag{2.269}$$

However, if $\nu_{\mathrm{n},k} = 0$ for some $k = 1, \ldots, \mathrm{n}_r$, this conversion does not hold, and another reference species has to be chosen. Accordingly, an affinity

$$\underset{\mathrm{s}}{\lambda}_k = \frac{1}{T}\sum_{\alpha=1}^{\mathrm{n}} \underset{\mathrm{s}}{\nu}_{\alpha,k} m_\alpha \underset{\mathrm{s}}{\mu}_\alpha \tag{2.270}$$

for surface reactions is defined, and thus

$$\underset{\mathrm{s}}{r}_{s,r} = -\sum_{k=1}^{\mathrm{n}_{\mathrm{s}}} \underset{\mathrm{s}}{q}_k \cdot \underset{\mathrm{s}}{\lambda}_k. \tag{2.271}$$

The local second law (in combination with the Curie principle) now states

$$\underset{\mathrm{s}}{r}_{s,r} \geq 0 \qquad \forall (\mathbf{x}, t) \in \Omega \times I \tag{2.272}$$

and one could ask which *thermodynamic ansatz* (TD ansatz)[14] for q_k is sufficient to ensure $\underset{\mathrm{s}}{r}_{s,r} \geq 0$. The following abbreviations are useful for the further derivation,

$$\underline{q} = (q_1, \ldots, q_{\mathrm{n}_r}) \tag{2.273}$$

$$\underline{\lambda} = (\lambda_1, \ldots, \lambda_{\mathrm{n}_r}) \tag{2.274}$$

with which one could write

$$r_{s,r} = \left\langle \underline{q}, \underline{\lambda} \right\rangle . \tag{2.275}$$

The most simple approach to ensures the second law is

$$\underline{q} = -\underline{\underline{\ell}} \cdot \underline{\lambda} \tag{2.276}$$

with a positive definite matrix $\underline{\underline{\ell}} \in \mathbb{R}^{\mathrm{n}_r \times \mathrm{n}_r}$. L. Onsager showed that the matrix $\underline{\underline{\ell}}$ is has to be symmetric [30, 31], for which he received the Nobel price in chemistry 1968. This *Onsager reciprocity* allows for a Cholesky decomposition

$$\underline{\underline{\ell}} = \underline{\underline{d}} \cdot \underline{\underline{d}}^{\mathrm{T}}, \tag{2.277}$$

with a lower triangle matrix $\underline{\underline{d}}$. The abbreviation

$$\underline{\lambda}' := \underline{\underline{d}} \cdot \underline{\lambda} \tag{2.278}$$

represents a linear combination of affinities. Hence one is able to write the entropy production as

$$r_{s,r} = \langle \underline{\lambda}', \underline{\lambda}' \rangle = \left|\left|\underline{\lambda}'\right|\right|^2 \geq 0. \tag{2.279}$$

Similar approaches are applied for the surface reaction rates (with equal definitions as above), *i.e.*

$$\underset{\mathrm{s}}{\underline{q}} = -\underset{\mathrm{s}}{\underline{\underline{\ell}}} \cdot \underset{\mathrm{s}}{\underline{\lambda}} \tag{2.280}$$

with a symmetric, positive definite matrix $\underset{\mathrm{s}}{\underline{\underline{\ell}}}$ and the decomposition $\underset{\mathrm{s}}{\underline{\underline{\ell}}} = \underset{\mathrm{s}}{\underline{\underline{d}}} \cdot \underset{\mathrm{s}}{\underline{\underline{d}}}^{\mathrm{T}}$. With

$$\underset{\mathrm{s}}{\underline{\lambda}'} = \underset{\mathrm{s}}{\underline{\underline{d}}} \cdot \underset{\mathrm{s}}{\underline{\lambda}} \tag{2.281}$$

one obtains

$$\underset{\mathrm{s}}{r}_{s,r} = \left|\left|\underset{\mathrm{s}}{\underline{\lambda}'}\right|\right|^2 \geq 0. \tag{2.282}$$

[14] Explicit representations of $q_k = q_k(\lambda_k)$ are called thermodynamic ansatz to clearly distinguish an actual model, *i.e.* a representation $\mu = \mu(T, \rho_1, \ldots, \rho_{\mathrm{n}})$.

2.7.2 Flux conditions

Reconsider the flux constraint

$$\sum_{\alpha=1}^{\mathrm{n}} \mathbf{j}_\alpha = \mathbf{0} \tag{2.283}$$

which was a consequence from the conservation of mass. With this, one is able to rewrite (*without loss of generality*) the flux entropy production as

$$r_{s,\mathbf{j}} = \mathbf{j}_u^{\mathrm{T}} \cdot \nabla \frac{1}{T} - \sum_{\alpha=1}^{\mathrm{n}} \mathbf{j}_\alpha^{\mathrm{T}} \cdot \left(\nabla \frac{\mu_\alpha}{T} - \frac{e_0 z_\alpha}{T\, m_\alpha} \mathbf{E} \right) \tag{2.284}$$

$$= \mathbf{j}_u^{\mathrm{T}} \cdot \nabla \frac{1}{T} - \sum_{\alpha=1}^{\mathrm{n}-1} \mathbf{j}_\alpha^{\mathrm{T}} \cdot \left(\nabla \frac{\mu_\alpha - \mu_{\mathrm{n}}}{T} - \frac{e_0}{T} \left(\frac{z_\alpha}{m_\alpha} - \frac{z_{\mathrm{n}}}{m_{\mathrm{n}}} \right) \mathbf{E} \right). \tag{2.285}$$

Of course, the reference to the nth species is arbitrary. However, it is not necessary to exploit the constraint $\sum_{\alpha=1}^{\mathrm{n}} \mathbf{j}_\alpha = \mathbf{0}$ at the very *beginning* of the flux derivation.

With $\mathbb{K} := \mathbb{R}^3$ It is convenient to define

$$\underline{\mathbf{j}} = \Big(-\mathbf{j}_u, \mathbf{j}_1, \ldots, \mathbf{j}_{\mathrm{n}-1} \Big) \qquad \in \mathbb{K}^{\mathrm{n}} \tag{2.286}$$

$$\underline{\boldsymbol{\gamma}} = \left(\nabla \frac{1}{T}, \nabla \frac{\mu_1 - \mu_{\mathrm{n}}}{T} - \frac{e_0}{T} \left(\frac{z_1}{m_1} - \frac{z_{\mathrm{n}}}{m_{\mathrm{n}}} \right) \mathbf{E}, \ldots \right. \tag{2.287}$$

$$\left. \ldots, \nabla \frac{\mu_{\mathrm{n}-1} - \mu_{\mathrm{n}}}{T} - \frac{e_0}{T} \left(\frac{z_{\mathrm{n}-1}}{m_{\mathrm{n}-1}} - \frac{z_{\mathrm{n}}}{m_{\mathrm{n}}} \right) \mathbf{E} \right) \qquad \in \mathbb{K}^{\mathrm{n}} \tag{2.288}$$

one is able to write the flux entropy production in the compact form

$$r_{s,\mathbf{j}} = -\underline{\mathbf{j}} \cdot \underline{\boldsymbol{\gamma}}^{\mathrm{T}}. \tag{2.289}$$

Note that $\underline{\mathbf{j}}_0 = -\mathbf{j}_u$. Similar to above, an approach for $\underline{\mathbf{j}}$ is desired which ensures $r_{s,\mathbf{j}} \geq 0$, and the most simple choice is clearly

$$\underline{\mathbf{j}} = -\underline{\boldsymbol{\gamma}} \cdot \underline{\underline{\mathbf{L}}} \tag{2.290}$$

with a positive definite matrix $\underline{\underline{\mathbf{L}}} \in \mathbb{K}^{\mathrm{n}\times\mathrm{n}}$.[15] Like in the reaction ansatz, this *linear*[16] relationship between the fluxes $\underline{\mathbf{j}}$ and the generalized thermodynamic forces $\underline{\boldsymbol{\lambda}}$ is doubtably for very high currents[32]. Nevertheless, throughout this work only linear relations of the type eq. (2.290) are considered.

Of course, a similar reciprocity condition on $\underline{\underline{\mathbf{L}}}$ as the symmetry of $\underline{\underline{\ell}}$ is desired. It is generally accepted that linear irreversible thermodynamics *postulates* [5, p. 203] this symmetry, while modern extensions of thermodynamics derive this symmetry. In addition, if magnetic contributions are present, the symmetry of the coefficients $\mathbf{L}_{\alpha,\beta}$ breaks down (in fact it becomes anti-symmetric [10, p. 73]). Since in my work the Onsager reciprocity is not the main focus, the following assumption is stated.

[15] Note that the entries $\mathbf{L}_{\alpha,\beta}$ of $\underline{\underline{\mathbf{L}}}$ are itself matrices, *i.e.* $\mathbf{L}_{\alpha,\beta} \in \mathbb{R}^{3\times3}$. However, the positive definite condition applies for the matrix *of matrices*.

[16] *Linear* means here a linear relationship between the fluxes $\underline{\mathbf{j}}$ and the forces $\underline{\boldsymbol{\lambda}}$. The explicit Onsager matrices $\mathbf{L}_{\alpha,\beta}$ are **not** necessarily constant or linear in the variables $(\rho u, \rho_1, \ldots, \rho_{\mathrm{n}})$, but (to some extend) arbitrary tensor valued functions.

Assumption 16 (Onsager coefficient symmetry)**.**

If no magnetic contributions are present, the elementary Onsager matrix $\mathbf{L}_{\alpha,\beta}$ is assumed to be **symmetric** and **positive definite**. It obeys the Cholesky decomposition

$$\underline{\underline{\mathbf{L}}} = \underline{\underline{\mathbf{D}}} \cdot \underline{\underline{\mathbf{D}}}^{\mathrm{T}}, \tag{2.291}$$

with a lower triangle matrix $\underline{\underline{\mathbf{D}}}$.

With the Cholesky decomposition one could further introduce the force combinations

$$\underline{\gamma}' = \underline{\underline{\mathbf{D}}} \cdot \underline{\gamma} \tag{2.292}$$

and write the flux entropy production as norm, *i.e.*

$$r_{s,\mathbf{j}} = \left\langle \underline{\gamma}', \underline{\gamma}' \right\rangle = \left\| \underline{\gamma}' \right\|^2 \geq 0. \tag{2.293}$$

Thus one has the explicit flux representation

$$\mathbf{j}_u = \mathbf{L}_{0,0} \cdot \nabla \frac{1}{T} + \sum_{\beta=1}^{\mathrm{n}-1} \mathbf{L}_{\beta,0} \cdot \nabla \frac{\mu_\beta - \mu_\mathrm{n}}{T} - \frac{e_0}{T} \left(\frac{z_\beta}{m_\beta} - \frac{z_\mathrm{n}}{m_\mathrm{n}} \right) \tag{2.294}$$

$$\mathbf{j}_\alpha = -\mathbf{L}_{0,\alpha} \cdot \nabla \frac{1}{T} - \sum_{\beta=1}^{\mathrm{n}-1} \mathbf{L}_{\alpha,\beta} \cdot \nabla \frac{\mu_\beta - \mu_\mathrm{n}}{T} - \frac{e_0}{T} \left(\frac{z_\beta}{m_\beta} - \frac{z_\mathrm{n}}{m_\mathrm{n}} \right) \tag{2.295}$$

and the symmetry condition states $\mathbf{L}_{\alpha,\beta} = \mathbf{L}_{\beta,\alpha},\ \alpha, \beta = 0, 1, \ldots, \mathrm{n}-1$.

Surfaces fluxes of course obey a similar derivation, which is, however, not given here. I will just postulate a symmetric and positive definite matrix $\underset{\mathrm{s}}{\mathbf{L}}_{\alpha,\beta}$ which relates the surface fluxes to the forces, *i.e.*

$$\underset{\mathrm{s}}{\mathbf{j}}_\alpha = \sum_{\alpha=1}^{\mathrm{n}} \underset{\mathrm{s}}{\mathbf{L}}_{\alpha,\beta} \cdot \left(\underset{\mathrm{s}}{\nabla} \frac{\underset{\mathrm{s}}{\mu_\alpha} - \underset{\mathrm{s}}{\mu_\mathrm{n}}}{T} - \frac{e_0}{\underset{\mathrm{s}}{T}} \cdot \left(\frac{z_\alpha}{m_\alpha} - \frac{z_\mathrm{n}}{m_\mathrm{n}} \right) \underset{\mathrm{s}}{\mathbf{E}} \right) \tag{2.296}$$

and ensures

$$\underset{\mathrm{s}}{r}_{s,\mathbf{j}} \geq 0 \quad \forall (\mathbf{x}, t) \in \Sigma \times I. \tag{2.297}$$

2.7.3 Equilibrium conditions

Before the equilibrium conditions are derived, thermodynamic states are introduced.

Definition 10 (Thermodynamic state)**.**

A solution of the coupled equation system (2.197),(2.202)-(2.205),(2.207) and (2.208) with respect to some boundary conditions is called thermodynamic state and abbreviated as

$$\underline{t}^Z := (\rho^Z(\mathbf{x}, t) u^Z(\mathbf{x}, t), \rho_1^Z(\mathbf{x}, t), \ldots, \rho_\mathrm{n}^Z(\mathbf{x}, t), \mathbf{D}^Z(\mathbf{x}, t), \mathbf{B}^Z(\mathbf{x}, t)). \tag{2.298}$$

The superscript ^{Z} should be understood as marker, *e.g.* $Z = \mathrm{Eq}$ for equilibrium or $Z = 0$ for the initial states at $t = 0$. Similar the surface state is defined as solution of the respective surface balance equations and consequently abbreviated as

$$\underset{\mathrm{s}}{\underline{t}}^Z := (\underset{\mathrm{s}}{u}^Z(\mathbf{x}, t), \underset{\mathrm{s}}{\rho_1^Z}(\mathbf{x}, t), \ldots, \underset{\mathrm{s}}{\rho_\mathrm{n}^Z}(\mathbf{x}, t)). \tag{2.299}$$

Note, however, that these thermodynamic states are yet formal solutions of the eq. system (2.197),(2.202)-(2.205),(2.207) and 2.208) as the boundary conditions are **not yet** specified. Recall that all thermodynamic potentials are functions of the independent fields, *e.g.* $\mu_\alpha = \mu_\alpha(\rho u, \rho_1, \ldots, \rho_\mathrm{n}, \mathbf{D}, \mathbf{B})$. One could thus insert the formal solutions $\underline{t}^Z$ to obtain the corresponding thermodynamic potentials of the state, *i.e.*

$$T(\underline{t}^Z) =: T^Z \tag{2.300}$$

$$\mu_\alpha(\underline{t}^Z) =: \mu_\alpha^Z \qquad \alpha = 1, \ldots, \mathrm{n} \tag{2.301}$$

$$\mathbf{P}(\underline{t}^Z) =: \mathbf{P}^Z \tag{2.302}$$

$$\mathbf{M}(\underline{t}^Z) =: \mathbf{M}^Z \tag{2.303}$$

and from the Gibbs equation

$$p(\underline{t}^Z) =: p^Z. \tag{2.304}$$

All of these thermodynamic potentials can be considered as *functionals*, *i.e.*

$$T^Z = T^Z[\rho u, \rho_1, \ldots, \rho_\mathrm{n}, \mathbf{D}, \mathbf{B}] \tag{2.305}$$

One could thus speak of the *temperature* T^Z *of state* Z or the *chemical potential* μ_α^Z *of state* Z. The same methodology is applied for the surface properties. Further, one could interpret the entropy production as functional

$$r_s = r_s[\underline{t}^Z] = r_s(T^Z, \mu_1^Z, \ldots, \mu_\mathrm{n}^Z) \tag{2.306}$$

and derive some general results on thermodynamic states. Specific boundary conditions then determine the actual functions.

Of special interest are of course thermodynamic states in which the entropy production vanishes. These are frequently called *equilibrium states*, however, the term is not consistently used in literature and hence defined for the following work.

Definition 11 (Thermodynamic equilibrium states)**.**

A thermodynamic state $\underline{t}^\mathrm{Eq}$ is called global equilibrium state if the total entropy production vanishes, *i.e.*

$$r_s[\underline{t}^\mathrm{Eq}] = 0, \tag{2.307}$$

and similar $\underset{\mathrm{s}}{\underline{t}}^\mathrm{Eq}$ is called global equilibrium state of the surface.

However, as not necessarily the overall entropy production has to vanish, one introduces (*partial*) equilibrium states, *i.e.*

- reaction equilibrium states $(\underline{t}^\ominus, \underset{\mathrm{s}}{\underline{t}}^\ominus)$ satisfying

$$r_{s,r}[\underline{t}^\ominus] = 0 \quad \text{and} \quad \underset{\mathrm{s}}{r}_{s,r}[\underset{\mathrm{s}}{\underline{t}}^\ominus] = 0, \tag{2.308}$$

- and flux equilibrium states $(\underline{t}^*, \underset{\mathrm{s}}{\underline{t}}^*)$ with

$$r_{s,\mathbf{j}}[\underline{t}^*] = 0 \quad \text{and} \quad \underset{\mathrm{s}}{r}_{s,\mathbf{j}}[\underset{\mathrm{s}}{\underline{t}}^*] = 0. \tag{2.309}$$

Reaction equilibrium

Consider now only the entropy production due to chemical reactions (either in the volume or on the surface) and the corresponding equilibrium state $\underline{t}^{\ominus}$. Equation (2.279) implies[17]

$$\underline{\lambda}'^{\ominus} = \underline{0} \tag{2.310}$$

and since $\underline{\lambda}' = \underline{\underline{d}} \cdot \underline{\lambda}$, with a lower triangle matrix $\underline{\underline{d}}$, a Gaussian elimination procedure leads (iteratively) to

$$\lambda_k = 0 \qquad \text{for } k = 1, \ldots, \mathrm{n}_r. \tag{2.311}$$

This is the well known **equilibrium condition for chemical reactions**

$$\sum_{\alpha=1}^{\mathrm{n}} \nu_{\alpha,k} m_\alpha \mu_\alpha^{\ominus} = 0 \qquad \text{for } k = 1, \ldots, \mathrm{n}_r, \tag{2.312}$$

and similar for surfaces

$$\sum_{\alpha=1}^{\mathrm{n}} \underset{\mathrm{s}}{\nu}_{\alpha,k} m_\alpha \underset{\mathrm{s}}{\mu}_\alpha^{\ominus} = 0 \qquad \text{for } k = 1, \ldots, \underset{\mathrm{s}}{\mathrm{n}}_r. \tag{2.313}$$

Flux equilibrium

The flux entropy production was also written as a norm of some linear combinations of the flux driving forces, *i.e.*

$$r_{s,\mathbf{j}} = \left\| \underline{\gamma}' \right\| \overset{!}{=} 0 \tag{2.314}$$

with

$$\underline{\gamma}' = \underline{\underline{\mathbf{D}}} \cdot \underline{\gamma}. \tag{2.315}$$

Similar, the equilibrium condition requires

$$\underline{\gamma}' = \underline{0} \tag{2.316}$$

and with a Gaussian elimination[18] one deduces

$$\nabla \frac{1}{T^*} = \mathbf{0} \tag{2.317}$$

$$\nabla \frac{\mu_\alpha^* - \mu_\mathrm{n}^*}{T^*} - \frac{e_0}{T^*} \left(\frac{z_\alpha}{m_\alpha} - \frac{z_\mathrm{n}}{m_\mathrm{n}} \right) \mathbf{E}^* = \mathbf{0} \qquad \text{for } \alpha = 1, \ldots, \mathrm{n}. \tag{2.318}$$

Note that the state $\underline{t}^*$ is itself a solution of a PDE system, and thus space dependent. The nabla operators in (2.317) hence operates on this (formal) solution.

[17] Note that more than one state could ensure a vanishing entropy production.

[18] Of course the Gaussian elimination requires the inevitability of each matrix $\mathbf{L}_{\alpha,\beta}$. However, Müller[5] actually starts its derivation of the reciprocity condition with some matrix $\mathbf{M}_{\alpha,\beta}$, which turns out to be a (linear combination) of $\mathbf{L}_{\alpha,\beta}^{-1}$. I thus fairly assume here that all Onsager coefficients are invertible.

2.8 Free energy

The intrinsic set of variables $(\rho\, u, \rho_1, \ldots, \rho_\mathrm{n})$ is (most often) not convenient to describe a thermodynamic system in laboratory situations. It is, however, possible to change this set of variables to another set of (more convenient) variables via two methodologies, *i.e.*

- variable changes
- and variable transformations.

While variable changes directly exchange a state variable, *e.g.* ρ_n with ρ, variable transformations exchange an extensive field with its corresponding (or conjugate) thermodynamic potential, *e.g.* ρ_n with μ_n. In this section I will briefly describe *variable changes* and *variable transformations* and motive thereby the introduction of the Helmholtz free energy and the Gibbs free energy.

Corollary 9 (Legendre transformation)**.**

Consider some function f which depends on u and satisfies

$$\frac{\partial\, f(u)}{\partial\, u} =: v \tag{2.319}$$

for which a **variable transformation** $u \rightsquigarrow v$ is desired. The independent variable u becomes a function (*i.e.* $u = u(v)$) and v the independent variable. One is then seeking the explicit representation

$$u = -\frac{\partial\, g(v)}{\partial\, v} \tag{2.320}$$

where g is to be determined. With $\widetilde{f} := f(u(v))$ the choice

$$g(v) = \widetilde{f}(v) - u(v)\, v = f(u(v)) - u(v)\, v \tag{2.321}$$

leads to

$$\frac{\partial\, (f(u(v)) - u\, v)}{\partial\, v} = \underbrace{\frac{\partial\, f(u)}{\partial\, u}}_{=v} \cdot \frac{\partial\, u(v)}{\partial\, v} - \frac{\partial\, u(v)}{\partial\, v} \cdot v - u \frac{\partial\, v}{\partial\, v} = -u \tag{2.322}$$

The function $g(v)$ is called **Legendre transformation** of f (with respect to (u, v)) and v is termed **conjugate variable** of u.

2.8.1 Helmholtz free energy

Suppose now that the Temperature T should become an independent degree of freedom. Temperature was introduced as

$$\frac{\partial\, \rho s}{\partial\, \rho u} = \frac{1}{T} \tag{2.323}$$

since ρs was supposed to be a function of ρu. However, due to the Gibbs equation (2.227) one could also write

$$\frac{\partial\, \rho u}{\partial\, \rho s} = T \tag{2.324}$$

and interpret the internal energy density as function of the entropy density, *i.e.*

$$\rho u = \mathfrak{u}(\rho s, \rho_1, \ldots, \rho_\mathrm{n}). \tag{2.325}$$

Performing a variable the transformation $\rho s \rightsquigarrow T$ and interpret ρs and T as conjugate variables entails a Legendre transformation of ρu.

Following the above corollary, the explicit representation $\rho s = \mathfrak{s}(T, \rho_1, \ldots, \rho_\mathrm{n})$ is obtained via

$$\mathfrak{s} = -\frac{\partial \mathfrak{f}(T, \rho_1, \ldots, \rho_\mathrm{n})}{\partial T} = \mathfrak{s}(T, \rho_1, \ldots, \rho_\mathrm{n}) \tag{2.326}$$

where $\mathfrak{f}$ is the Legendre transformation of ρu (with respect to $(\rho s, T)$). Its explicit representation is also obtained from the corollary and has the familiar shape

$$\mathfrak{f} = \rho u - T\rho s =: \rho\psi. \tag{2.327}$$

This Legendre transformation is further called (Helmholtz) **free energy** and $\mathfrak{f}$ **material function**. Clearly, the representation of the internal energy $\mathfrak{u}(T, \rho_1, \ldots, \rho_\mathrm{n})$ is obtained as

$$\mathfrak{u} = \mathfrak{f} - T\frac{\partial \mathfrak{f}}{\partial T} = \mathfrak{u}(T, \rho_1, \ldots, \rho_\mathrm{n}). \tag{2.328}$$

The investigation of the entropy balance now starts with

$$\frac{\partial \mathfrak{f}(T, \rho_1, \ldots, \rho_\mathrm{n})}{\partial t} = \frac{\partial \mathfrak{f}}{\partial T} \cdot \frac{\partial T}{\partial t} + \sum_{\alpha=1}^{\mathrm{n}} \frac{\partial \mathfrak{f}}{\partial \rho_\alpha} \cdot \frac{\partial \rho_\alpha}{\partial t}. \tag{2.329}$$

Due to the representation

$$\mathfrak{f} = \rho u - T\rho s \tag{2.330}$$

one also obtains

$$\frac{\partial \mathfrak{f}}{\partial t} = \frac{\partial \rho u}{\partial t} - T\frac{\partial \rho s}{\partial t} - \rho s\frac{\partial T}{\partial t} = \frac{\partial \rho u}{\partial t} - T\frac{\partial \rho s}{\partial t} + \frac{\partial \mathfrak{f}}{\partial T}\frac{\partial T}{\partial t} \tag{2.331}$$

and thus

$$T\frac{\partial \rho s}{\partial t} = \frac{\partial \rho u}{\partial t} - \sum_{\alpha=1}^{\mathrm{n}} \frac{\partial \mathfrak{f}}{\partial \rho_\alpha} \cdot \frac{\partial \rho_\alpha}{\partial t}. \tag{2.332}$$

A comparison to the (elementary) entropy balance

$$\frac{\partial \rho s}{\partial t} = \frac{1}{T}\frac{\partial \rho u}{\partial t} - \sum_{\alpha=1}^{\mathrm{n}} \frac{\mu_\alpha}{T} \cdot \frac{\partial \rho_\alpha}{\partial t} \tag{2.333}$$

identifies the chemical potential μ_α as

$$\frac{\partial \mathfrak{f}}{\partial \rho_\alpha} = \mu_\alpha(T, \rho_1, \ldots, \rho_\mathrm{n}). \tag{2.334}$$

Note that the different sets of variables, here either $(\rho u, \rho_1, \ldots, \rho_\mathrm{n})$ or $(T, \rho_1, \ldots, \rho_\mathrm{n})$, determines the actual thermodynamic potential (either ρs or $\rho\psi$) as origin of a driving force, *i.e.*

- the chemical potential $\mu_\alpha(\rho u, \rho_1, \ldots, \rho_\mathrm{n})$ with

$$\frac{\partial\, \mathfrak{s}(\rho u, \rho_1, \ldots, \rho_\mathrm{n})}{\partial\, \rho_\alpha} = \mu_\alpha(\rho u, \rho_1, \ldots, \rho_\mathrm{n}) \tag{2.335}$$

- or the chemical potential $\mu_\alpha(T, \rho_1, \ldots, \rho_\mathrm{n})$ with

$$\frac{\partial\, \mathfrak{f}(T, \rho_1, \ldots, \rho_\mathrm{n})}{\partial\, \rho_\alpha} = \mu_\alpha(T, \rho_1, \ldots, \rho_\mathrm{n}). \tag{2.336}$$

Another consequence of the variable transformation $\rho s \rightsquigarrow T$ is the representation of the energy balance. The Legendre transformation $\mathfrak{f} = \rho u - T\rho s$ lead to

$$\mathfrak{u}(T, \rho_1, \ldots, \rho_\mathrm{n}) = \mathfrak{f}(T, \rho_1, \ldots, \rho_\mathrm{n}) + T\frac{\partial\, \mathfrak{f}(T, \rho_1, \ldots, \rho_\mathrm{n})}{\partial\, T}. \tag{2.337}$$

Comparing hence

$$\frac{\partial\, \rho u}{\partial\, t} = \frac{\partial\, \mathfrak{u}(T, \rho_1, \ldots, \rho_\mathrm{n})}{\partial\, t} = \frac{\partial\, (\mathfrak{f} - T\mathfrak{s})}{\partial\, t} \stackrel{!}{=} -\mathrm{div}\,(\mathfrak{u}\mathbf{v} + \mathbf{j}_u) + r_u \tag{2.338}$$

and applying the auxiliary calculation 2.28 leads to the **heat equation**

$$\begin{aligned} C_T \cdot \frac{\partial\, T}{\partial\, t} =& -\,\mathrm{div}\,\left(\left(\frac{\partial\, \mathfrak{f}}{\partial\, T} - \sum_{\alpha=1}^{\mathrm{n}} \frac{\partial\, \mu_\alpha}{\partial\, T}\rho_\alpha\right) \cdot \mathbf{v} + \frac{1}{T}\left(\mathbf{j}_u - \sum_{\alpha=1}^{\mathrm{n}} (\mu_\alpha - T\,\frac{\partial\, \mu_\alpha}{\partial\, T})\,\mathbf{j}_\alpha\right)\right) \\ & - \left(\sum_{\alpha=1}^{\mathrm{n}} \rho_\alpha \nabla \frac{\partial\, \mu_\alpha}{\partial\, T}\right) \cdot \mathbf{v}^{\mathrm{T}} - \sum_{\alpha=1}^{\mathrm{n}} (\frac{\mu_\alpha}{T} - \frac{\partial\, \mu_\alpha}{\partial\, T}) \cdot r_k \\ & + \mathbf{j}_u^{\mathrm{T}} \cdot \nabla \frac{1}{T} - \sum_{\alpha=1}^{\mathrm{n}} \mathbf{j}_\alpha^{\mathrm{T}} \cdot \left(\nabla \frac{\mu_\alpha}{T} - \nabla \frac{\partial\, \mu_\alpha}{\partial\, T} - \frac{e_0 z_\alpha}{T\, m_\alpha}\mathbf{E}\right) \\ =& -\,\mathrm{div}\,(\rho\vartheta\mathbf{v} + \mathbf{j}_\vartheta) + r_\vartheta \end{aligned} \tag{2.339}$$

where

- $C_T = \frac{\partial^2 \mathfrak{f}}{\partial T}$ is the specific heat capacity,
- $\mathfrak{s}_\alpha = \frac{\partial^2 \mathfrak{f}}{\partial T \partial \rho_\alpha} = \frac{\partial\, \mathfrak{s}}{\partial\, \rho_\alpha} = \frac{\partial\, \mu_\alpha}{\partial\, T}$ the molar entropy,
- $\vartheta(T, \rho_1, \ldots, \rho_\mathrm{n}) = \rho^{-1}\mathfrak{s} - \sum_{\alpha=1}^{\mathrm{n}} w_\alpha \mathfrak{s}_\alpha$ is called heat density with units $\left[\frac{\mathrm{J}}{\mathrm{m}^3}\right]$,
- $\mathbf{j}_\vartheta = \frac{1}{T}\left(\mathbf{j}_u - \sum_{\alpha=1}^{\mathrm{n}} (\mu_\alpha - T\,\frac{\partial\, \mu_\alpha}{\partial\, T})\,\mathbf{j}_\alpha\right)$ heat flux ,
- and

$$\begin{aligned} r_\vartheta =& -\left(\sum_{\alpha=1}^{\mathrm{n}} \rho_\alpha \nabla \frac{\partial\, \mu_\alpha}{\partial\, T}\right) \cdot \mathbf{v} - \sum_{\alpha=1}^{\mathrm{n}} (\frac{\mu_\alpha}{T} - \frac{\partial\, \mu_\alpha}{\partial\, T}) \cdot r_k + \nabla \frac{1}{T} \cdot \mathbf{j}_u^{\mathrm{T}} \\ & - \mathbf{j}_\alpha^{\mathrm{T}} \cdot \left(\nabla \frac{\mu_\alpha}{T} - \nabla \frac{\partial\, \mu_\alpha}{\partial\, T} - \frac{e_0 z_\alpha}{T\, m_\alpha}\mathbf{E}\right) \end{aligned}$$

  is termed heat source.

Auxiliary calculation 2.28:

$$
\begin{aligned}
\frac{\partial \rho u}{\partial t} &= \frac{\partial \mathfrak{u}(T,\rho_1,\ldots,\rho_\mathrm{n})}{\partial t} = \frac{\partial \left(\mathfrak{f}(T,\rho_1,\ldots,\rho_\mathrm{n}) - T\mathfrak{s}(T,\rho_1,\ldots,\rho_\mathrm{n})\right)}{\partial t} \\
&= \frac{\partial \mathfrak{f}}{\partial T}\cdot\frac{\partial T}{\partial t} + \sum_{\alpha=1}^{\mathrm{n}} \frac{\partial \mathfrak{f}}{\partial \rho_\alpha}\cdot\frac{\partial \rho_\alpha}{\partial t} - \frac{\partial T}{\partial t}\mathfrak{s} - T\frac{\partial \mathfrak{s}}{\partial T}\frac{\partial T}{\partial t} - T\sum_{\alpha=1}^{\mathrm{n}}\frac{\partial \mathfrak{s}}{\partial \rho_\alpha}\cdot\frac{\partial \rho_\alpha}{\partial t} \\
&= \sum_{\alpha=1}^{\mathrm{n}} \mu_\alpha\cdot\frac{\partial \rho_\alpha}{\partial t} + T\underbrace{\frac{\partial^2 \mathfrak{f}}{\partial^2 T}}_{=:C_T}\cdot\frac{\partial T}{\partial t} - T\sum_{\alpha=1}^{\mathrm{n}}\underbrace{\frac{\partial \mu_\alpha}{\partial T}}_{=:\mathfrak{s}_\alpha}\cdot\frac{\partial \rho_\alpha}{\partial t}
\end{aligned}
$$

Dividing the whole equation by T leads to

$$
\begin{aligned}
C_T\cdot\frac{\partial T}{\partial t} &= \underbrace{\frac{1}{T}\frac{\partial \rho u}{\partial t} - \sum_{\alpha=1}^{\mathrm{n}}\frac{\mu_\alpha}{T}\cdot\frac{\partial \rho_\alpha}{\partial t}}_{=-\mathrm{div}\,(\rho s\mathbf{v}+\mathbf{j}_s)+r_s} + \sum_{\alpha=1}^{\mathrm{n}}\frac{\partial \mu_\alpha}{\partial T}\cdot\frac{\partial \rho_\alpha}{\partial t} \\
&= -\,\mathrm{div}\left(\frac{\partial \mathfrak{f}}{\partial T}\cdot\mathbf{v} + \frac{1}{T}\left(\mathbf{j}_u - \sum_{\alpha=1}^{\mathrm{n}}\mu_\alpha\,\mathbf{j}_\alpha\right)\right) + r_s \\
&\quad - \sum_{\alpha=1}^{\mathrm{n}}\mathfrak{s}_\alpha\cdot\left(\mathrm{div}\,(\rho_\alpha\mathbf{v}+\mathbf{j}_\alpha) - r_\alpha\right) \\
&\overset{\text{eq.(2.226)}}{=} -\,\mathrm{div}\left(\left(\frac{\partial \mathfrak{f}}{\partial T} - \sum_{\alpha=1}^{\mathrm{n}}\mathfrak{s}_\alpha\rho_\alpha\right)\cdot\mathbf{v} + \frac{1}{T}\left(\mathbf{j}_u - \sum_{\alpha=1}^{\mathrm{n}}(\mu_\alpha - T\mathfrak{s}_\alpha)\,\mathbf{j}_\alpha\right)\right) \\
&\quad - \left(\sum_{\alpha=1}^{\mathrm{n}}\rho_\alpha\nabla\mathfrak{s}_\alpha\right)\cdot\mathbf{v} - \sum_{\alpha=1}^{\mathrm{n}}\left(\frac{\mu_\alpha}{T} - \mathfrak{s}_\alpha\right)\cdot r_k \\
&\quad - \sum_{\alpha=1}^{\mathrm{n}}\mathbf{j}_\alpha\cdot\left(\nabla\frac{\mu_\alpha}{T} - \nabla\mathfrak{s}_\alpha - \frac{e_0 z_\alpha}{T\,m_\alpha}\mathbf{E}\right)
\end{aligned}
$$

The heat equation obeys also the alternative balance representation

$$
C_T\cdot\frac{\partial T}{\partial t} = -\mathrm{div}\,(\rho\widetilde{\vartheta}\mathbf{v} + \mathbf{j}_s) + r_{\widetilde{\vartheta}} \tag{2.340}
$$

in which $\widetilde{\vartheta} = s = -\rho^{-1}\frac{\partial \mathfrak{f}}{\partial T}$ is interpreted as the specific heat and

$$
\mathbf{j}_{\widetilde{\vartheta}} = \mathbf{j}_s \tag{2.341}
$$

$$
r_{\widetilde{\vartheta}} = r_s - \sum_{\alpha=1}^{\mathrm{n}}\left(\mathrm{div}\,(\rho_\alpha\mathbf{v}+\mathbf{j}_\alpha) - r_\alpha\right)\cdot\frac{\partial \mu_\alpha}{\partial T}. \tag{2.342}
$$

Of course, both representations are equal and the *appropriate* one is chosen according to the boundary conditions. If one could state from a physical point of view why, *e.g.*

$$
\oint_{\partial\Omega}\mathbf{j}_s\cdot d\mathbf{A} = 0, \tag{2.343}
$$

the second representation is more convenient.

2.8.2 Gibbs free energy

Yet another Legendre transformation is obtained by choosing p as an independent degree of freedom. First, note that

$$\rho\psi = \mathfrak{f}(T, \rho_1, \ldots, \rho_\mathrm{n}) = \mathfrak{f}(T, \rho \cdot w_1, \ldots, \rho \cdot w_{\mathrm{n}-1}, \rho \cdot (1 - \sum_{\alpha=1}^{\mathrm{n}-1} w_\alpha)) \tag{2.344}$$

and thus one could interpret the set $(T, \rho, w_1, \ldots, w_{\mathrm{n}-1})$ as independent variables. A variable *exchange* $(T, \rho_1, \ldots, \rho_\mathrm{n}) \to (T, \rho, w_1, \ldots, w_{\mathrm{n}-1})$ which is **not** part of a Legendre transformation is simply called **variable change**, in contrast to a variable transformation (*i.e.* Legendre transformation). With $v = \rho^{-1}$ one calculates (*c.f.* the following auxiliary calculation)

$$\frac{\partial\,\psi}{\partial\,v} = -p \tag{2.345}$$

and consequently identifies $-p$ as the conjugate variable of ρ^{-1}.

Auxiliary calculation 2.29:

$$\begin{aligned}
\frac{\partial\,\psi}{\partial\,\rho} = \frac{\partial\,(\rho\psi \cdot \rho^{-1})}{\partial\,\rho} &= \frac{\partial\,(\mathfrak{f}(T, \rho \cdot w_1, \ldots, \rho \cdot w_{\mathrm{n}-1}, \rho\,(1 - \sum_{\alpha=1}^{\mathrm{n}-1} w_\alpha)) \cdot \rho^{-1})}{\partial\,\rho} \\
&= \sum_{\alpha=1}^{\mathrm{n}} \frac{\partial\,\mathfrak{f}}{\partial\,\rho_\alpha} \cdot \frac{\partial\,\rho w_\alpha}{\partial\,\rho}\rho^{-1} + \mathfrak{f} \cdot \frac{\partial\,\rho^{-1}}{\partial\,\rho} \\
&= \rho^{-2} \cdot \Big(\underbrace{\sum_{\alpha=1}^{\mathrm{n}} \mu_\alpha \rho_\alpha - \rho\psi}_{=-p \text{ (Gibbs eq. 2.227)}} \Big)
\end{aligned}$$

Thus, the variable transformation $\rho^{-1} \rightsquigarrow p$ implies the Legendre transformation

$$g = \psi + p\rho^{-1} \tag{2.346}$$

with

$$\frac{\partial\,g}{\partial\,p} = \rho^{-1}. \tag{2.347}$$

Due to the Gibbs equation the Legendre transformation g (of ψ) satisfies

$$g = \psi + pv = u - T\,s + p\,v = \sum_{\alpha=1}^{\mathrm{n}} \mu_\alpha w_\alpha \tag{2.348}$$

and is further called **Gibbs free energy** density. The explicit representation

$$g = \mathfrak{g}(T, p, w_1, \ldots, w_{\mathrm{n}-1}) \tag{2.349}$$

is called **material function** of g.

Note the crucial difference between g and $\rho\psi$ and their respective material functions.

While the material function of $\mathfrak{g}$ has units $\left[\frac{\mathrm{J}}{\mathrm{kg}}\right]$ (the mass density is factored out)[19], the material function of $\mathfrak{f}$ of $\rho\psi$ has units $\left[\frac{\mathrm{J}}{\mathrm{m}^3}\right]$. The respective global energies are

$$G = \int_\Omega \rho g \, dV = \int_\Omega \rho \mathfrak{g}(T, p, w_1, \ldots, w_{n-1}) \, dV \tag{2.350}$$

$$F = \int_\Omega \rho\psi \, dV = \int_\Omega \mathfrak{f}(T, \rho_1, \ldots, \rho_\mathrm{n}) \, dV \tag{2.351}$$

if no surface contributions are considered. Hence, if a material function $\mathfrak{g}^*$ is given, satisfying

$$G = \int_\Omega \mathfrak{g}^* \, dV, \tag{2.352}$$

the Gibbs free energy density is simply $\mathfrak{g} = \rho^{-1}\mathfrak{g}^*$.

The entropy function $s = \mathfrak{s}$ is obtained from

$$\mathfrak{s} = -\frac{\partial \mathfrak{g}(T, p, w_1, \ldots, w_{\mathrm{n}-1})}{\partial T} = \mathfrak{s}(T, p, w_1, \ldots, w_{\mathrm{n}-1}) \tag{2.353}$$

and g is thus also a Legendre transformation of u with respect to s. The representation of $u = \mathfrak{u}$ is given by

$$\mathfrak{u} = \mathfrak{g} - T\frac{\partial \mathfrak{g}}{\partial T} - p\frac{\partial \mathfrak{g}}{\partial p} = \mathfrak{u}(T, p, w_1, \ldots, w_{\mathrm{n}-1}). \tag{2.354}$$

Again, the entropy balance is employed to derive the representation of the chemical potential. Due to the representation $g = u - T\,s + p\,v$ and with the subsequent auxiliary calculations one deduces

$$\frac{\partial \rho\mathfrak{g}}{\partial t} = \frac{\partial \rho u}{\partial t} - \frac{\partial (T\rho s)}{\partial t} + \frac{\partial p}{\partial t} \tag{2.355}$$

$$\Leftrightarrow \quad \frac{\partial \rho s}{\partial t} = \frac{1}{T} \cdot \left(\frac{\partial \rho u}{\partial t} + \frac{\partial \rho\mathfrak{g}}{\partial t} - \frac{\partial p}{\partial t} - \rho s \frac{\partial T}{\partial t}\right) \tag{2.356}$$

$$= \frac{1}{T} \cdot \frac{\partial \rho u}{\partial t} + \sum_{\alpha=1}^{\mathrm{n}-1} \frac{1}{T} \left(\frac{\partial \mathfrak{g}}{\partial w_\alpha} + (\mathfrak{g} - \frac{\partial \mathfrak{g}}{\partial w_\alpha}) \cdot w_\alpha\right) \cdot \frac{\partial \rho_\alpha}{\partial t} \tag{2.357}$$

$$+ \left(\sum_{\alpha=1}^{\mathrm{n}-1} \frac{1}{T}(\mathfrak{g} - \frac{\partial \mathfrak{g}}{\partial w_\alpha}) \cdot w_\alpha\right) \cdot \frac{\partial \rho_\mathrm{n}}{\partial t}. \tag{2.358}$$

[19] Since $\rho > 0$ this could always be performed

Auxiliary calculation 2.30:

$$\begin{aligned}
\frac{\partial \rho \mathfrak{g}}{\partial t} &= \mathfrak{g}\frac{\partial \rho}{\partial t} + \rho\frac{\partial \mathfrak{g}}{\partial T}\cdot\frac{\partial T}{\partial t} + \rho\frac{\partial \mathfrak{g}}{\partial p}\frac{\partial p}{\partial t} + \rho\sum_{\alpha=1}^{\mathrm{n}-1}\frac{\partial \mathfrak{g}}{\partial w_\alpha}\cdot\frac{\partial w_\alpha}{\partial t} \\
&= \rho\mathfrak{s}\frac{\partial T}{\partial t} + \frac{\partial p}{\partial t} + \sum_{\alpha=1}^{\mathrm{n}-1}\frac{\partial \mathfrak{g}}{\partial w_\alpha}\cdot\frac{\partial \rho_\alpha}{\partial t} + \left(\mathfrak{g} - \sum_{\beta=1}^{\mathrm{n}-1}\frac{\partial \mathfrak{g}}{\partial w_\beta}w_\beta\right)\cdot\frac{\partial \rho}{\partial t} \\
&= \rho\mathfrak{s}\frac{\partial T}{\partial t} + \frac{\partial p}{\partial t} + \sum_{\alpha=1}^{\mathrm{n}-1}\left(\frac{\partial \mathfrak{g}}{\partial w_\alpha} + \left(\mathfrak{g} - \sum_{\beta=1}^{\mathrm{n}-1}\frac{\partial \mathfrak{g}}{\partial w_\beta}w_\beta\right)\right)\cdot\frac{\partial \rho_\alpha}{\partial t} \\
&\quad + \left(\mathfrak{g} - \sum_{\beta=1}^{\mathrm{n}-1}\frac{\partial \mathfrak{g}}{\partial w_\beta}w_\beta\right)\cdot\frac{\partial \rho_\mathrm{n}}{\partial t}
\end{aligned}$$

A comparison to the elementary entropy function

$$\frac{\partial \rho s}{\partial t} = \frac{1}{T}\frac{\partial \rho u}{\partial t} - \sum_{\alpha=1}^{\mathrm{n}}\frac{\mu_\alpha}{T}\cdot\frac{\partial \rho_\alpha}{\partial t} \tag{2.359}$$

leads to the representations

$$\mu_\alpha(T,p,w_1,\ldots,w_{\mathrm{n}-1}) = \left(\frac{\partial \mathfrak{g}}{\partial w_\alpha} + \left(\mathfrak{g} - \sum_{\beta=1}^{\mathrm{n}-1}\frac{\partial \mathfrak{g}}{\partial w_\beta}w_\beta\right)\right) \qquad \alpha = 1,\ldots,\mathrm{n}-1 \tag{2.360}$$

$$\mu_\mathrm{n}(T,p,w_1,\ldots,w_{\mathrm{n}-1}) = \left(\mathfrak{g} - \sum_{\beta=1}^{\mathrm{n}-1}\frac{\partial \mathfrak{g}}{\partial w_\beta}w_\beta\right) \tag{2.361}$$

of the chemical potential. However, one could also write

$$\mu_\alpha = \frac{\partial \mathfrak{g}}{\partial w_\alpha} + \mu_\mathrm{n} \tag{2.362}$$

or simply

$$\frac{\partial \mathfrak{g}}{\partial w_\alpha} = \mu_\alpha - \mu_\mathrm{n} \qquad \alpha = 1,\ldots,\mathrm{n}. \tag{2.363}$$

This is quite remarkable if one reconsiders the driving force of a flux, *i.e.*

$$\boldsymbol{\gamma}_\alpha = \nabla\frac{\mu_\alpha - \mu_\mathrm{n}}{T} - \frac{e_0}{T}\cdot\left(\frac{z_\alpha}{m_\alpha} - \frac{z_\mathrm{n}}{m_\mathrm{n}}\right)\mathbf{E} \qquad \alpha = 1,\ldots,\mathrm{n}-1. \tag{2.364}$$

Obviously, the (thermodynamic part) of the driving force is proportional to the gradient of $T^{-1}\frac{\partial \mathfrak{g}}{\partial w_\alpha}$ and the force may be written as

$$\boldsymbol{\gamma}_\alpha = \nabla\left(\frac{1}{T}\frac{\partial \mathfrak{g}}{\partial w_\alpha}\right) - \frac{e_0}{T}\cdot\left(\frac{z_\alpha}{m_\alpha} - \frac{z_\mathrm{n}}{m_\mathrm{n}}\right)\mathbf{E} \qquad \alpha = 1,\ldots,\mathrm{n}-1. \tag{2.365}$$

This circumstance is sometimes used in literature to interpret

$$\frac{\partial \mathfrak{g}}{\partial w_\alpha} = \mu_\alpha^* \tag{2.366}$$

as chemical potential. Clearly, one could set up a thermodynamic theory where μ_α^* is actually the chemical potential, as long as all other derived properties are defined accordingly.

In chemistry yet another set of variables is quite common, *i.e.* $(T, p, c_1, \ldots, c_{\mathrm{n}-1})$ with the mole fraction

$$c_\alpha = \frac{n_\alpha}{\sum_{\beta=1}^{\mathrm{n}} n_\beta} \qquad \alpha = 1, \ldots, \mathrm{n}. \tag{2.367}$$

Thus, consider the variable change $(T, p, w_1, \ldots, w_{\mathrm{n}-1}) \to (T, p, c_1, \ldots, c_{\mathrm{n}-1})$ with

$$c_\alpha(w_1, \ldots, w_{\mathrm{n}-1}) = \frac{m_\alpha^{-1} w_\alpha}{m_{\mathrm{n}}^{-1} + \sum_{\gamma=1}^{\mathrm{n}-1} (m_\gamma^{-1} - m_{\mathrm{n}}^{-1})\, w_\gamma} \tag{2.368}$$

$$\sum_{\gamma=1}^{\mathrm{n}} m_\gamma^{-1} w_\gamma = \frac{n}{\rho} \tag{2.369}$$

and

$$\frac{\partial\, c_\alpha}{\partial\, w_\beta} = m_\alpha^{-1} \frac{\rho}{n} \cdot \left(\delta_{\alpha,\beta} + w_\alpha \frac{\rho}{n} (m_{\mathrm{n}}^{-1} - m_\beta^{-1}) \right). \tag{2.370}$$

Auxiliary calculation 2.31:

$$\begin{aligned}
\frac{\partial\, c_\alpha}{\partial\, w_\beta} &= \frac{m_\alpha^{-1} w_\alpha}{\sum_{\gamma=1}^{\mathrm{n}} m_\gamma^{-1} w_\gamma} + \frac{m_\alpha^{-1} w_\alpha}{(\sum_{\gamma=1}^{\mathrm{n}} m_\gamma^{-1} w_\gamma)^2} \cdot \sum_{\gamma=1}^{\mathrm{n}-1} (m_{\mathrm{n}}^{-1} - m_\gamma^{-1}) \frac{\partial\, w_\gamma}{\partial\, w_\beta} \\
&= m_\alpha^{-1} \frac{\rho}{n} \cdot \delta_{\alpha,\beta} + m_\alpha^{-1} w_\alpha \frac{\rho^2}{n^2} \cdot \sum_{\gamma=1}^{\mathrm{n}-1} (m_{\mathrm{n}}^{-1} - m_\gamma^{-1}) \delta_{\gamma,\beta}
\end{aligned}$$

With AC 2.32 the chemical potentials μ_{n} and $\overline{\mu}_\alpha$ in the variables $(T, p, c_1, \ldots, c_{\mathrm{n}-1})$ are

$$\mu_{\mathrm{n}} = \mathfrak{g} - \sum_{\beta=1}^{\mathrm{n}-1} \frac{\partial\, \mathfrak{g}}{\partial\, w_\beta} w_\beta \tag{2.371}$$

$$= \widetilde{\mathfrak{g}} - \frac{\rho}{n} m_{\mathrm{n}}^{-1} \sum_{\beta=1}^{\mathrm{n}-1} \frac{\partial\, \widetilde{\mathfrak{g}}}{\partial\, c_\beta} c_\beta \tag{2.372}$$

$$= \mu_{\mathrm{n}}(T, p, c_1, \ldots, c_{\mathrm{n}-1}) \tag{2.373}$$

and

$$\mu_\alpha = \frac{1}{T} \left(\frac{\partial\, \mathfrak{g}}{\partial\, w_\alpha} - \sum_{\beta=1}^{\mathrm{n}-1} \frac{\partial\, \mathfrak{g}}{\partial\, w_\beta} w_\beta + \mathfrak{g} \right) \tag{2.374}$$

$$= \frac{1}{T} \left(\frac{\partial\, \widetilde{\mathfrak{g}}}{\partial\, c_\alpha} m_\alpha^{-1} \frac{\rho}{n} - m_\beta^{-1} \frac{\rho}{n} \sum_{\beta=1}^{\mathrm{n}-1} \frac{\partial\, \widetilde{\mathfrak{g}}}{\partial\, c_\beta} c_\beta + \widetilde{\mathfrak{g}} \right) \tag{2.375}$$

$$= \mu_\alpha(T, p, c_1, \ldots, c_{\mathrm{n}-1}). \tag{2.376}$$

Auxiliary calculation 2.32:

$$\sum_{\beta=1}^{\mathrm{n}-1} \frac{\partial\, \mathfrak{g}}{\partial\, w_\beta} w_\beta = \sum_{\beta=1}^{\mathrm{n}-1} \sum_{\alpha=1}^{\mathrm{n}-1} \frac{\partial\, \widetilde{\mathfrak{g}}}{\partial\, c_\alpha} \cdot \frac{\partial\, c_\alpha}{\partial\, w_\beta} w_\beta = \sum_{\alpha=1}^{\mathrm{n}-1} \frac{\partial\, \widetilde{\mathfrak{g}}}{\partial\, c_\alpha} \sum_{\beta=1}^{\mathrm{n}-1} w_\beta \frac{\partial\, c_\alpha}{\partial\, w_\beta}$$

$$= \sum_{\alpha=1}^{\mathrm{n}-1} \frac{\partial\, \widetilde{\mathfrak{g}}}{\partial\, c_\alpha} m_\alpha^{-1} \frac{\rho}{n} \sum_{\beta=1}^{\mathrm{n}-1} w_\beta \cdot \left(\delta_{\alpha,\beta} + w_\alpha \frac{\rho}{n}(m_\mathrm{n}^{-1} - m_\beta^{-1})\right)$$

Side calculation:

$$\sum_{\beta=1}^{\mathrm{n}-1} w_\beta w_\alpha \frac{\rho}{n}(m_\mathrm{n}^{-1} - m_\beta^{-1}) = w_\alpha \frac{\rho}{n} m_\mathrm{n}^{-1} \sum_{\beta=1}^{\mathrm{n}-1} w_\beta - w_\alpha \frac{\rho}{n} \sum_{\beta=1}^{\mathrm{n}-1} w_\beta m_\beta^{-1}$$

$$= w_\alpha \frac{\rho}{n} m_\mathrm{n}^{-1}(1 - w_\mathrm{n}) - w_\alpha \frac{\rho}{n} \sum_{\beta=1}^{\mathrm{n}-1} w_\beta m_\beta^{-1} = w_\alpha \frac{\rho}{n} m_\mathrm{n}^{-1} - w_\alpha \frac{\rho}{n} \sum_{\beta=1}^{\mathrm{n}} w_\beta m_\beta^{-1}$$

$$= w_\alpha \frac{\rho}{n} m_\mathrm{n}^{-1} - w_\alpha \sum_{\beta=1}^{\mathrm{n}} c_\beta = w_\alpha \frac{\rho}{n} m_\mathrm{n}^{-1} - w_\alpha$$

Insertion leads to

$$\sum_{\beta=1}^{\mathrm{n}-1} \frac{\partial\, \mathfrak{g}}{\partial\, w_\beta} w_\beta = \sum_{\alpha=1}^{\mathrm{n}-1} \frac{\partial\, \widetilde{\mathfrak{g}}}{\partial\, c_\alpha} m_\alpha^{-1} \frac{\rho}{n} \left(w_\alpha + w_\alpha \frac{\rho}{n} m_\mathrm{n}^{-1} - w_\alpha\right) = \frac{\rho}{n} m_\mathrm{n}^{-1} \sum_{\alpha=1}^{\mathrm{n}-1} \frac{\partial\, \widetilde{\mathfrak{g}}}{\partial\, c_\alpha} c_\alpha$$

The Gibbs free energy density is then modeled **per particle**, and not per mass, *i.e.*

$$G = \int_\Omega n \cdot \overline{g}\, dV = \int_\Omega n \cdot \overline{\mathfrak{g}}(T, p, c_1, \ldots, c_{\mathrm{n}-1}) \tag{2.377}$$

with a material function $\overline{g} = \overline{\mathfrak{g}}(T, p, c_1, \ldots, c_{\mathrm{n}-1})$. The density $\overline{g}$ is called species density of the Gibbs energy. Hence, the density with respect to mass is simply

$$g = \frac{n}{\rho} \cdot \overline{g} \tag{2.378}$$

and the material function of g is

$$\widetilde{\mathfrak{g}}(T, p, c_1, \ldots, c_{\mathrm{n}-1}) = \frac{n}{\rho} \cdot \overline{\mathfrak{g}}(T, p, c_1, \ldots, c_{\mathrm{n}-1}). \tag{2.379}$$

Since

$$\frac{\rho}{n} = \sum_{\alpha=1}^{\mathrm{n}-1} (m_\alpha - m_\mathrm{n}) c_\alpha \tag{2.380}$$

one obtains

$$\frac{\partial\, \overline{\mathfrak{g}}}{\partial\, c_\beta} = \frac{\partial\, (\frac{\rho}{n} \cdot \widetilde{\mathfrak{g}})}{\partial\, c_\beta} = \frac{\rho}{n} \frac{\partial\, \widetilde{\mathfrak{g}}}{\partial\, c_\beta} + \widetilde{\mathfrak{g}}(m_\alpha - m_\mathrm{n}). \tag{2.381}$$

Note further that for the Gibbs energy per particle $\overline{g}$ the (inverse) number density n^{-1} is

the conjugate variable of p, *i.e.*

$$\frac{\partial \overline{g}}{\partial p} = \frac{\partial \widetilde{\mathfrak{g}} \cdot \frac{\rho}{n}}{\partial p} = \frac{\rho}{n}\frac{\partial \widetilde{\mathfrak{g}}}{\partial p} = \frac{\rho}{n} v = n^{-1} =: \overline{v}(T, p, c_1, \ldots, c_{\mathrm{n}-1}) \tag{2.382}$$

as with eq. (2.380) the expression $\frac{\rho}{n}$ is independent of p. $\overline{v}$ is called specific volume with respect to the amount of particles. The material function representations of the entropy $\mathfrak{s}$ and the internal energy $\mathfrak{u}$ are

$$\overline{\mathfrak{s}}(T, p, c_1, \ldots, c_{\mathrm{n}-1}) = \frac{\partial \overline{\mathfrak{g}}}{\partial T} = \frac{n}{\rho}\mathfrak{s} \tag{2.383}$$

$$\overline{\mathfrak{u}}(T, p, c_1, \ldots, c_{n-1}) = \overline{\mathfrak{g}} - T\frac{\partial \overline{\mathfrak{g}}}{\partial T} - p\frac{\partial \overline{\mathfrak{g}}}{\partial p} = \frac{n}{\rho}\mathfrak{u}. \tag{2.384}$$

Quite similar to above a compact expression for $m_\alpha \mu_\alpha - m_{\mathrm{n}}\mu_{\mathrm{n}}$ is deduced, *i.e.*

$$m_\alpha \mu_\alpha - m_{\mathrm{n}}\mu_{\mathrm{n}} = \frac{\partial \overline{\mathfrak{g}}}{\partial c_\alpha} \tag{2.385}$$

and

$$\mu_{\mathrm{n}}(T, p, c_1, \ldots, c_{\mathrm{n}-1}) = \frac{1}{m_{\mathrm{n}}}\left(\overline{\mathfrak{g}} - \sum_{\alpha=1}^{\mathrm{n}-1}\frac{1}{T}\frac{\partial \overline{\mathfrak{g}}}{\partial c_\alpha} \cdot c_\alpha\right) \tag{2.386}$$

$$\mu_\alpha(T, p, c_1, \ldots, c_{\mathrm{n}-1}) = \frac{1}{m_\alpha}\left(\frac{\partial \overline{\mathfrak{g}}}{\partial c_\alpha} - \sum_{\beta=1}^{\mathrm{n}-1}\frac{\partial \overline{\mathfrak{g}}}{\partial c_\beta} \cdot c_\beta + \overline{\mathfrak{g}}\right). \tag{2.387}$$

Auxiliary calculation 2.33:

$$\begin{aligned} m_\alpha \mu_\alpha - m_{\mathrm{n}}\mu_{\mathrm{n}} &= \left(\frac{\rho}{n}\frac{\partial \widetilde{\mathfrak{g}}}{\partial c_\alpha} - \frac{\rho}{n}\sum_{\beta=1}^{\mathrm{n}-1}\frac{\partial \widetilde{\mathfrak{g}}}{\partial c_\beta}c_\beta + m_\alpha \widetilde{\mathfrak{g}}\right) - \left(m_{\mathrm{n}}\widetilde{\mathfrak{g}} - \frac{\rho}{n}\sum_{\beta=1}^{\mathrm{n}-1}\frac{\partial \widetilde{\mathfrak{g}}}{\partial c_\beta}c_\beta\right) \\ &= \frac{\rho}{n}\frac{\partial \widetilde{\mathfrak{g}}}{\partial c_\alpha} + (m_\alpha - m_{\mathrm{n}}) \cdot \widetilde{\mathfrak{g}} = \frac{\partial \overline{\mathfrak{g}}}{\partial c_\alpha} \end{aligned}$$

Recalling the affinity

$$\lambda_k = \frac{1}{T}\sum_{\alpha=1}^{\mathrm{n}} \nu_{\alpha,k} m_\alpha \mu_\alpha \tag{2.388}$$

and the equilibrium condition for chemical reactions

$$\sum_{\alpha=1}^{\mathrm{n}} \nu_{\alpha,k}\overline{\mu}_\alpha^{\ominus} = 0. \tag{2.389}$$

If the number of particles is conserved in each reaction, *i.e.* $\sum_{\alpha=1}^{\mathrm{n}} \nu_{\alpha,k} = 0$ the equilibrium

condition is indeed

$$\sum_{\alpha=1}^{\mathrm{n}-1} \nu_{\alpha,k}(\overline{\mu}_\alpha^\ominus - \overline{\mu}_\mathrm{n}^\ominus) = 0 \tag{2.390}$$

$$\sum_{\alpha=1}^{\mathrm{n}-1} \nu_{\alpha,k} \frac{\partial\, \mathfrak{g}^\ominus}{\partial\, c_\alpha} = 0, \tag{2.391}$$

which seems somehow reasonable as the pressure remains in such circumstances constant. Interpreting the material function $\mathfrak{g}(T, p, c_1, \ldots, c_{\mathrm{n}-1})$ as as functional $\mathfrak{g}[\underline{t}^Z]$ shows that the equilibrium state $\underline{t}^\ominus$ is the minimum of $\mathfrak{g}$ with respect to the *directions* $\underline{\nu}_k = (\nu_{1,k}, \ldots, \nu_{\mathrm{n}-1,k})$, *i.e.*

$$\mathrm{D}\,(\mathfrak{g})(\underline{\nu}_k) = \sum_{\alpha=1}^{\mathrm{n}-1} \nu_{\alpha,k} \frac{\partial\, \mathfrak{g}}{\partial\, c_\alpha} \stackrel{!}{=} 0 \qquad k = 1, \ldots, \mathrm{n}_r, \tag{2.392}$$

where $\mathrm{D}\,(\mathfrak{g})(\underline{\nu_k})$ denotes the Frechet derivative. This could also be written as *linear* equation system

$$\underline{\underline{\nu}} \cdot \underline{\mu} = \mathbf{0} \qquad \in \mathbb{R}^{\mathrm{n}_r} \tag{2.393}$$

with

$$\underline{\underline{\nu}} = \begin{pmatrix} \nu_{1,1} & \cdots & \nu_{\mathrm{n}-1,1} \\ \cdots & \ddots & \cdots \\ \nu_{1,\mathrm{n}_r} & \cdots & \nu_{\mathrm{n}-1,\mathrm{n}_r} \end{pmatrix} \qquad \in \mathbb{R}^{\mathrm{n}_r \times (\mathrm{n}-1)} \tag{2.394}$$

$$\underline{\mu} = (\overline{\mu}_\alpha - \overline{\mu}_\mathrm{n})_{\alpha=1,\ldots,\mathrm{n}-1} = (\frac{\partial\, \mathfrak{g}}{\partial\, c_\alpha})_{\alpha=1,\ldots,\mathrm{n}-1} \qquad \in \mathbb{R}^{(\mathrm{n}-1)}. \tag{2.395}$$

Clearly, since $\underline{\underline{\nu}}$ is not even quadratic matrix, there is not necessarily one unique solution, if any. If there are more reactions than species present, $\mathrm{n}_r \geq \mathrm{n} - 1$, there exits, however, at least an approximation **state** $\underline{t}^{\mathrm{LS}}$ satisfying

$$\left|\left|\underline{\underline{\nu}} \cdot \underline{\mu}^{\mathrm{LS}}\right|\right| = \min_{\underline{\mu} \in \mathbb{R}^{\mathrm{n}-1}} \left|\left|\underline{\underline{\nu}} \cdot \underline{\mu}\right|\right|. \tag{2.396}$$

This least squares approximation is then called Gibbs energy minimizing state.

The chemical potentials per particle $\overline{\mu}_\alpha$ also arise in the flux conditions. Since the entropy production (without polarization) is

$$\frac{\partial\, \rho s}{\partial\, t} = \frac{1}{T} \frac{\partial\, \rho u}{\partial\, t} - \sum_{\alpha=1}^{\mathrm{n}} \frac{\partial\, \mu_\alpha}{\partial\, T} \frac{\partial\, \rho_\alpha}{\partial\, t} \tag{2.397}$$

one could of course write $\frac{\partial\, \rho_\alpha}{\partial\, t} = m_\alpha \frac{\partial\, n_\alpha}{\partial\, t}$ and thus shift m_α to the μ_α-term. Consequently, the entropy balance is

$$\frac{\partial\, \rho s}{\partial\, t} = \frac{1}{T} \frac{\partial\, \rho u}{\partial\, t} - \sum_{\alpha=1}^{\mathrm{n}} \frac{\partial\, \overline{\mu}_\alpha}{\partial\, T} \frac{\partial\, n_\alpha}{\partial\, t} \tag{2.398}$$

with $\overline{\mu}_\alpha$ as thermodynamic driving force. While μ_α is the chemical potential of species α per mass (*i.e.* units $\left[\frac{\mathrm{J}}{\mathrm{kg}}\right]$), $\overline{\mu}_\alpha$ denotes the chemical potential per mole (or per particle)

with units $\left[\frac{\mathrm{J}}{\mathrm{mol}}\right]$ (or $[\,\mathrm{J}\,]$).

The difference $\mu_\alpha - \mu_\mathrm{n}$ as driving force arose essentially due to the frame of reference in which the balance equation of mass is a conservation equation, *i.e.*

$$\frac{\partial\,\rho}{\partial\,t} = -\mathrm{div}\,(\rho\mathbf{v}) \tag{2.399}$$

$$\sum_{\alpha=1}^{\mathrm{n}} \mathbf{j}_\alpha = \mathbf{0}. \tag{2.400}$$

Choosing now a coordinate system $\mathbf{y} \in \Omega$ which satisfies

$$\frac{\partial\,n(\mathbf{y},t)}{\partial\,t} = -\mathrm{div}\,(n(\mathbf{y},t)\overline{\mathbf{v}}(\mathbf{y},t)) + \underbrace{\sum_{\alpha=1}^{\mathrm{n}} \overline{r}_\alpha}_{:=\overline{r}} \tag{2.401}$$

$$\sum_{\alpha=1}^{\mathrm{n}} m_\alpha \mathbf{j}_\alpha = \mathbf{0} \tag{2.402}$$

leads to the particle flux

$$\bar{\mathbf{j}}_\alpha(\mathbf{y},t) = m_\alpha \cdot \mathbf{j}_\alpha(\mathbf{y},t) \tag{2.403}$$

and the corresponding balance equation of the species density n_α, *i.e.*

$$\frac{\partial\,n_\alpha(\mathbf{y},t)}{\partial\,t} = -\mathrm{div}\,(n\overline{\mathbf{v}}(\mathbf{y},t) + \bar{\mathbf{j}}_\alpha(\mathbf{y},t)) + \overline{r}_\alpha(\mathbf{y},t) \tag{2.404}$$

$$\overline{r}_\alpha = \sum_{k=1}^{\mathrm{n}_r} \nu_{\alpha,k} \cdot q_k(\mathbf{y},t) \qquad \alpha = 1,\ldots,\mathrm{n}. \tag{2.405}$$

Since the total diffusive mass flux does not vanish in this frame of reference, it is

$$\mathbf{j}(\mathbf{y},t) = \sum_{\alpha=1}^{\mathrm{n}} \mathbf{j}_\alpha(\mathbf{y},t) = \sum_{\alpha=1}^{\mathrm{n}} m_\alpha \bar{\mathbf{j}}_\alpha(\mathbf{y},t) \tag{2.406}$$

and the mass balance is

$$\frac{\partial\,\rho}{\partial\,t} = -\mathrm{div}\,(\rho\overline{\mathbf{v}} + \mathbf{j}) = -\mathrm{div}\,(\rho\overline{\mathbf{v}} + \sum_{\alpha=1}^{\mathrm{n}} m_\alpha \bar{\mathbf{j}}_\alpha). \tag{2.407}$$

Note that the momentum of matter is now also represented as

$$\mathbf{p}_\mathrm{M}(\mathbf{y},t) = \rho(\mathbf{y},t)\mathbf{v}(\mathbf{y},t) + \mathbf{j} = \rho(\mathbf{y},t)\overline{\mathbf{v}}(\mathbf{y},t) + \sum_{\alpha=1}^{\mathrm{n}} m_\alpha \bar{\mathbf{j}}_\alpha(\mathbf{y},t) \tag{2.408}$$

and the balance equation has to be rewritten accordingly. However, since in the further work only models are considered where the momentum balance decouples, I will only state the internal energy balance in this frame of reference (since it is required to derive the entropy balance)

$$\frac{\partial\,\rho(\mathbf{y},t)u(\mathbf{y},t)}{\partial\,t} = -\mathrm{div}\,(\rho u\overline{\mathbf{v}} + \bar{\mathbf{j}}_u) + \overline{r}_u \tag{2.409}$$

$$\overline{r}_u = -\boldsymbol{\sigma} \bullet \boldsymbol{\nabla}\overline{\mathbf{v}} + \bar{\mathbf{j}}^\mathrm{F} \cdot \mathbf{E}^\mathrm{T} \tag{2.410}$$

without further derivation.

Inserting the balance equations, expressed in the coordinate system $\mathbf{y} \in \Omega$, in the entropy balance (2.398), and applying the flux constraint

$$\sum_{\alpha=1}^{\mathrm{n}} \bar{\mathbf{j}}_\alpha = \mathbf{0} \tag{2.411}$$

leads to

$$\frac{\partial \rho s}{\partial t} = \frac{\partial 1}{\partial T}\frac{\rho u}{t} - \sum_{\alpha=1}^{\mathrm{n}} \frac{\mu_\alpha}{T}\frac{\partial \rho_\alpha}{\partial t} \tag{2.412}$$

$$= -\mathrm{div}\,(\rho s \overline{\mathbf{v}} + \bar{\mathbf{j}}_s) \tag{2.413}$$

$$+ \bar{\mathbf{j}}_u^{\mathrm{T}} \cdot \nabla \frac{1}{T} - \sum_{\alpha=1}^{\mathrm{n}-1} \bar{\mathbf{j}}_\alpha^{\mathrm{T}} \cdot \left(\frac{\overline{\mu}_\alpha - \overline{\mu}_{\mathrm{n}}}{T} - \frac{e_0(z_\alpha - z_{\mathrm{n}})}{T}\mathbf{E} \right) - \sum_{k=1}^{\mathrm{n}_r} \lambda_k q_k \tag{2.414}$$

where all variables $(T, p, c_1, \ldots, c_{n-1})$ are functions of $(\mathbf{y}, t) \in \Omega \times I$.

Auxiliary calculation 2.34:

$$\frac{\partial \rho\, s(\mathbf{y},t)}{\partial u} = \frac{\partial 1}{\partial T}\frac{\rho u(\mathbf{y},t)}{t} - \sum_{\alpha=1}^{\mathrm{n}} \frac{m_\alpha \mu_\alpha}{T}\frac{\partial\, n_\alpha(\mathbf{y},t)}{\partial t}$$

$$= -\mathrm{div}\,(\rho s \overline{\mathbf{v}} + \bar{\mathbf{j}}_s)$$

$$+ \nabla \frac{1}{T} \cdot \bar{\mathbf{j}}_u^{\mathrm{T}} - \sum_{\alpha=1}^{\mathrm{n}} \bar{\mathbf{j}}_\alpha \cdot \left(\frac{m_\alpha \mu_\alpha}{T} - \frac{e_0\, z_\alpha}{T}\mathbf{E} \right) - \sum_{\alpha=1}^{\mathrm{n}} \frac{m_\alpha \mu_\alpha}{T} \overline{r}_\alpha$$

With the abbreviation

$$\underline{\overline{\gamma}} = \left(-\nabla \frac{1}{T}, \nabla \frac{\overline{\mu}_1 - \overline{\mu}_{\mathrm{n}}}{T} - \frac{e_0\,(z_1 - z_{\mathrm{n}})}{T}\mathbf{E}, \ldots, \nabla \frac{\overline{\mu}_{\mathrm{n}-1} - \overline{\mu}_{\mathrm{n}}}{T} - \frac{e_0\,(z_{\mathrm{n}-1} - z_{\mathrm{n}})}{T}\mathbf{E} \right) \tag{2.415}$$

$$\underline{\bar{\mathbf{j}}} = (\mathbf{j}_u, \bar{\mathbf{j}}_1, \ldots, \bar{\mathbf{j}}_{\mathrm{n}-1}) \tag{2.416}$$

the flux entropy production is

$$r_{s,\mathbf{j}} = \underline{\bar{\mathbf{j}}} \cdot \underline{\overline{\gamma}}^{\mathrm{T}}. \tag{2.417}$$

Clearly, a similar thermodynamic approach as in eq. (2.290) is now chosen for $\underline{\bar{\mathbf{j}}}$, *i.e.*

$$\underline{\mathbf{j}} = \underline{\underline{\overline{\mathbf{L}}}} \cdot \underline{\overline{\gamma}} \tag{2.418}$$

with a positive definite definite Matrix $\underline{\underline{\overline{\mathbf{L}}}}$, called Onsager matrix for the $(\mathbf{y}, \overline{\mathbf{v}})$ coordinate system.

Theorem 9 (Symmetry of alternative Onsager matrices)**.**

Let

$$\underline{\mathbf{j}} = \underline{\underline{\mathbf{M}}} \cdot \underline{\bar{\mathbf{j}}} \tag{2.419}$$

with an invertible matrix $\underline{\underline{\mathbf{M}}}$ called flux transformation matrix. **If** the Onsager matrix $\underline{\underline{\mathbf{L}}}$,

with

$$\underline{\mathbf{j}} = \underline{\underline{\mathbf{L}}} \cdot \underline{\gamma} \tag{2.420}$$

is symmetric, then the Onsager Matrix $\overline{\underline{\underline{\mathbf{L}}}}$ representing

$$\underline{\bar{\mathbf{j}}} = \overline{\underline{\underline{\mathbf{L}}}} \cdot \underline{\overline{\gamma}} \tag{2.421}$$

in the $(\mathbf{y}, \overline{\mathbf{v}})$ coordinate system is also symmetric and has the explicit representation

$$\overline{\underline{\underline{\mathbf{L}}}} = \underline{\underline{\mathbf{M}}}^{-1} \cdot \underline{\underline{\mathbf{L}}} \cdot \underline{\underline{\mathbf{M}}}^{-\mathrm{T}} \tag{2.422}$$

Proof. The flux entropy production obeys

$$r_{s,\mathbf{j}} = \left\langle \underline{\bar{\mathbf{j}}}, \underline{\overline{\gamma}} \right\rangle = \left\langle \underline{\underline{\mathbf{M}}} \cdot \underline{\mathbf{j}}, \underline{\overline{\gamma}} \right\rangle = \left\langle \underline{\mathbf{j}}, \underline{\underline{\mathbf{M}}}^{\mathrm{T}} \cdot \underline{\overline{\gamma}} \right\rangle \tag{2.423}$$

Since the entropy production is independent of the desired coordinate system, it holds

$$\left\langle \underline{\mathbf{j}}, \underline{\underline{\mathbf{M}}}^{\mathrm{T}} \cdot \underline{\overline{\gamma}} \right\rangle \stackrel{!}{=} \left\langle \underline{\mathbf{j}}, \underline{\gamma} \right\rangle \tag{2.424}$$

and thus

$$\underline{\gamma} = \underline{\underline{\mathbf{M}}}^{\mathrm{T}} \cdot \underline{\overline{\gamma}}. \tag{2.425}$$

With

$$\underline{\overline{\gamma}}^{\mathrm{T}} \cdot \overline{\underline{\underline{\mathbf{L}}}} \cdot \underline{\overline{\gamma}} = \underline{\gamma} \cdot \underline{\underline{\mathbf{M}}} \cdot \overline{\underline{\underline{\mathbf{L}}}} \cdot \underline{\underline{\mathbf{M}}}^{\mathrm{T}} \underline{\gamma} \stackrel{!}{=} \underline{\gamma}^{\mathrm{T}} \cdot \underline{\underline{\mathbf{L}}} \cdot \underline{\gamma} \tag{2.426}$$

one obtains the representation

$$\overline{\underline{\underline{\mathbf{L}}}} = \underline{\underline{\mathbf{M}}}^{-1} \cdot \underline{\underline{\mathbf{L}}} \cdot \underline{\underline{\mathbf{M}}}^{-\mathrm{T}} \tag{2.427}$$

and

$$\overline{\underline{\underline{\mathbf{L}}}}^{\mathrm{T}} = (\underline{\underline{\mathbf{M}}}^{-1} \cdot \underline{\underline{\mathbf{L}}} \cdot \underline{\underline{\mathbf{M}}}^{-\mathrm{T}})^{\mathrm{T}} = \underline{\underline{\mathbf{M}}}^{-1} \cdot \underline{\underline{\mathbf{L}}}^{\mathrm{T}} \cdot \underline{\underline{\mathbf{M}}}^{-\mathrm{T}} = \underline{\underline{\mathbf{M}}}^{-1} \cdot \underline{\underline{\mathbf{L}}} \cdot \underline{\underline{\mathbf{M}}}^{-\mathrm{T}} = \overline{\underline{\underline{\mathbf{L}}}} \tag{2.428}$$

shows that $\overline{\underline{\underline{\mathbf{L}}}}$ is indeed symmetric. □

Expectably, the symmetry principle of the Onsager matrix is independent of the actual frame of reference, and the equilibrium conditions are equal, which stated by the following corollary.

Corollary 10 (Equivalent equilibrium conditions)**.**
The equilibrium condition for the flux entropy production implies

$$\left\| \underline{\gamma}' \right\| = 0 \tag{2.429}$$

and thus $\underline{\gamma} = \mathbf{0}$. Since $\overline{\underline{\underline{\mathbf{L}}}}$ is symmetric, there exits also a Cholesky decomposition $\overline{\underline{\underline{\mathbf{L}}}} = \overline{\underline{\underline{\mathbf{D}}}} \cdot \overline{\underline{\underline{\mathbf{D}}}}^{\mathrm{T}}$ for which a vanishing flux entropy production

$$\left\| \overline{\underline{\underline{\mathbf{D}}}} \cdot \underline{\overline{\gamma}} \right\| = 0 \tag{2.430}$$

entails $\overline{\underline{\underline{\mathbf{D}}}} \cdot \underline{\overline{\gamma}} = \mathbf{0}$ and thus $\underline{\overline{\gamma}} = \mathbf{0}$ with a Gaussian elimination.

Remark 8 (Equilibrium condition in various frames of reference).
Note that the two equivalent equilibrium conditions

$$\nabla_{\mathbf{x}} \frac{\mu_\alpha - \mu_{\mathrm{n}}}{T} - \frac{e_0}{T}\left(\frac{z_\alpha}{m_\alpha} - \frac{z_{\mathrm{n}}}{m_{\mathrm{n}}}\right)\mathbf{E}(\mathbf{x},t) \stackrel{!}{=} 0 \qquad \alpha = 1,\ldots,\mathrm{n}-1 \tag{2.431}$$

$$\nabla_{\mathbf{y}} \frac{\overline{\mu}_\alpha - \overline{\mu}_{\mathrm{n}}}{T} - \frac{e_0\,(z_\alpha - z_{\mathrm{n}})}{T}\mathbf{E}(\mathbf{y},t) \stackrel{!}{=} 0 \qquad \alpha = 1,\ldots,\mathrm{n}-1 \tag{2.432}$$

are to be understood in their respective coordinate system.

2.8.3 Pressure and heat equation

The balance equation for the concentration c_α in the $(\mathbf{y}, \overline{\mathbf{v}})$ coordinate system is simply

$$\frac{\partial\, c_\alpha}{\partial\, t} = -\mathrm{div}\,(c_\alpha \overline{\mathbf{v}} + n^{-1}\bar{\mathbf{j}}_\alpha) - n^{-1}(\nabla n)\cdot\bar{\mathbf{j}}_\alpha + n^{-1}\cdot(\overline{r}_\alpha - c_\alpha\cdot\overline{r}). \tag{2.433}$$

Quite similar to the heat equation, which was obtained from the internal energy balance and the variable transformation $\rho s \rightsquigarrow T$, a pressure equation is deduced from the total species density balance. Since

$$n^{-1} = \frac{\partial\,\overline{\mathfrak{g}}}{\partial\, p} = \overline{v}(T, p, c_1, \ldots, c_{\mathrm{n}-1}) \tag{2.434}$$

the total species density balance leads to the pressure equation

$$\kappa_p \frac{\partial\, p}{\partial\, t} = \kappa_T \cdot \frac{\partial\, T}{\partial\, t} + \sum_{\alpha=1}^{\mathrm{n}} \kappa_\alpha \frac{\partial\, n_\alpha}{\partial\, t} \tag{2.435}$$

with the material coefficients

- thermal expansion coefficient $\kappa_T := n\frac{\partial\,\overline{v}}{\partial\, T} = \frac{\partial^2\overline{\mathfrak{g}}}{\partial p \partial T}$
- compressibility $\kappa_p := -n\frac{\partial\,\overline{v}}{\partial\, p} = -\frac{\partial^2\overline{\mathfrak{g}}}{\partial^2 p}$
- and specific species compressibility κ_α with

$$\kappa_\alpha = n\frac{\partial^2\overline{\mathfrak{g}}}{\partial p \partial c_\alpha} + \frac{\partial\,\overline{\mathfrak{g}}}{\partial\, p} - \sum_{\beta=1}^{\mathrm{n}-1} n\frac{\partial^2\overline{\mathfrak{g}}}{\partial p \partial c_\beta} c_\beta \quad \alpha = 1,\ldots,\mathrm{n}-1 \tag{2.436}$$

$$\kappa_{\mathrm{n}} = \frac{\partial\,\overline{\mathfrak{g}}}{\partial\, p} - \sum_{\beta=1}^{\mathrm{n}-1} n\frac{\partial^2\overline{\mathfrak{g}}}{\partial p \partial c_\beta} c_\beta. \tag{2.437}$$

Auxiliary calculation 2.35:

$$\frac{\partial n}{\partial t} = -n^2 \frac{\partial \overline{v}}{\partial t} = -n^2 \cdot \left(\frac{\partial \overline{v}}{\partial T} \cdot \frac{\partial T}{\partial t} + \frac{\partial \overline{v}}{\partial p} \frac{\partial p}{\partial t} + \sum_{\alpha=1}^{\mathrm{n}-1} \frac{\partial \overline{v}}{\partial c_\alpha} \cdot \frac{\partial c_\alpha}{\partial t} \right)$$

$$= -n \cdot \left(\underbrace{n \cdot \frac{\partial^2 \overline{\mathfrak{g}}}{\partial T \partial p}}_{=:\kappa_T} \cdot \frac{\partial T}{\partial t} + \underbrace{n \cdot \frac{\partial^2 \overline{\mathfrak{g}}}{\partial^2 p}}_{=:-\kappa_p} \cdot \frac{\partial p}{\partial t} + \sum_{\alpha=1}^{\mathrm{n}-1} n \cdot \frac{\partial^2 \mathfrak{g}}{\partial c_\alpha \partial p} \cdot \frac{\partial c_\alpha}{\partial t} \right)$$

Side calculation:

$$n^{-1} \cdot \frac{\partial n}{\partial t} + n \sum_{\alpha=1}^{\mathrm{n}} n \frac{\partial \overline{v}}{\partial c_\alpha} \cdot \left(\frac{\partial n_\alpha}{\partial t} - c_\alpha \frac{\partial n}{\partial t} \right)$$

$$= \left(\frac{\partial \overline{\mathfrak{g}}}{\partial p} + \sum_{\beta=1}^{\mathrm{n}-1} n \frac{\partial^2 \overline{\mathfrak{g}}}{\partial p \partial c_\beta} c_\beta \right) \frac{\partial n}{\partial t} - \sum_{\alpha=1}^{\mathrm{n}-1} n \frac{\partial^2 \overline{\mathfrak{g}}}{\partial p \partial c_\alpha} \cdot \frac{\partial n_\alpha}{\partial t}$$

$$= \left(\underbrace{\frac{\partial \overline{\mathfrak{g}}}{\partial p} - \sum_{\beta=1}^{\mathrm{n}-1} n \frac{\partial^2 \overline{\mathfrak{g}}}{\partial p \partial c_\beta} c_\beta}_{=:\kappa_n} \right) \frac{\partial n_{\mathrm{n}}}{\partial t} + \sum_{\alpha=1}^{\mathrm{n}-1} \left(\underbrace{n \frac{\partial^2 \overline{\mathfrak{g}}}{\partial p \partial c_\alpha} + \frac{\partial \overline{\mathfrak{g}}}{\partial p} - \sum_{\beta=1}^{\mathrm{n}-1} n \frac{\partial^2 \overline{\mathfrak{g}}}{\partial p \partial c_\beta} c_\beta}_{=:\kappa_\alpha} \right) \cdot \frac{\partial n_\alpha}{\partial t}$$

$$= \kappa_{\mathrm{n}} \cdot \frac{\partial n_{\mathrm{n}}}{\partial t} + \sum_{\alpha=1}^{\mathrm{n}-1} \kappa_\alpha \cdot \frac{\partial n_\alpha}{\partial t} = \sum_{\alpha=1}^{\mathrm{n}} \kappa_\alpha \cdot \frac{\partial n_\alpha}{\partial t}$$

Rearrangement of the above species density balance leads to the pressure equation

$$\kappa_p \frac{\partial p}{\partial t} = \kappa_T \cdot \frac{\partial T}{\partial t} + \sum_{\alpha=1}^{\mathrm{n}} \kappa_\alpha \frac{\partial n_\alpha}{\partial t}$$

The heat and pressure balance are coupled as in both equations $\frac{\partial p}{\partial t}$ and $\frac{\partial T}{\partial t}$ terms arise. The (lengthy) auxiliary calculation 2.36, however, decouples both equations and one obtains the **heat equation**

$$\begin{aligned} -(C_T + \kappa_p^{-1} \cdot \kappa_T^2) \cdot \frac{\partial T}{\partial t} = & -\mathrm{div}\,(n\vartheta\,\overline{\mathbf{v}} + \overline{\mathbf{j}}_\theta) - \sum_{\alpha=1}^{\mathrm{n}} \left(\frac{\overline{\mathfrak{h}}_\alpha}{T} - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha \right) \cdot \overline{r}_\alpha \\ & + \sum_{\alpha=1}^{\mathrm{n}} \overline{\mathbf{j}}_\alpha^{\mathrm{T}} \cdot \left(\nabla \left(\frac{\overline{\mathfrak{h}}_\alpha}{T} - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha \right) - \frac{e_0\, z_\alpha}{T} \mathbf{E} \right) \\ & - \left(\sum_{\alpha=1}^{\mathrm{n}} n_\alpha \nabla (\overline{\mathfrak{s}}_\alpha - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha) \right) \cdot \overline{\mathbf{v}}^{\mathrm{T}} \end{aligned} \tag{2.438}$$

with

- the heat ϑ as

$$\vartheta := \mathfrak{s} - \sum_{\alpha=1}^{\mathrm{n}} (\overline{\mathfrak{s}}_\alpha - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha) \cdot c_\alpha) = \vartheta(T, p, c_1, \ldots, c_{\mathrm{n}-1}) \tag{2.439}$$

- the corresponding heat flux $\bar{\mathbf{j}}_\vartheta$

$$\bar{\mathbf{j}}_\vartheta := (\bar{\mathbf{j}}_s - \sum_{\alpha=1}^{\mathrm{n}} (\bar{\mathfrak{s}}_\alpha - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha) \cdot \bar{\mathbf{j}}_\alpha) \tag{2.440}$$

$$= (\frac{1}{T} \left(\mathbf{j}_u - \sum_{\alpha=1}^{\mathrm{n}} \overline{\mu}_\alpha \bar{\mathbf{j}}_\alpha \right) - \sum_{\alpha=1}^{\mathrm{n}} (\bar{\mathfrak{s}}_\alpha - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha) \cdot \bar{\mathbf{j}}_\alpha) \tag{2.441}$$

$$= (\frac{1}{T} \mathbf{j}_u - \frac{1}{T} \sum_{\alpha=1}^{\mathrm{n}} (\bar{\mathfrak{h}}_\alpha - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha) \cdot \bar{\mathbf{j}}_\alpha) \tag{2.442}$$

- the specific enthalpy (see the derivation in auxiliary calculation 2.37)

$$\bar{\mathfrak{h}}_\alpha = \bar{\mathfrak{g}} - T \frac{\partial \bar{\mathfrak{g}}}{\partial T} - \sum_{\beta=1}^{\mathrm{n}-1} \left(\frac{\partial \bar{\mathfrak{g}}}{\partial c_\beta} - T \frac{\partial \bar{\mathfrak{g}}}{\partial T \partial c_\beta} \right) c_\beta + \frac{\partial \bar{\mathfrak{g}}}{\partial c_\alpha} - T \frac{\partial \bar{\mathfrak{g}}}{\partial T \partial c_\alpha} \quad \alpha = 1, \ldots, \mathrm{n}-1 \tag{2.443}$$

$$\bar{\mathfrak{h}}_\mathrm{n} = \bar{\mathfrak{g}} - T \frac{\partial \bar{\mathfrak{g}}}{\partial T} - \sum_{\beta=1}^{\mathrm{n}-1} \left(\frac{\partial \bar{\mathfrak{g}}}{\partial c_\beta} - T \frac{\partial \bar{\mathfrak{g}}}{\partial T \partial c_\beta} \right) c_\beta \tag{2.444}$$

- and the heat capacity $C_T = \frac{\partial^2 \mathfrak{g}}{\partial^2 T}$.

Recall the definition of the specific entropy[20], *i.e.* $\frac{\partial \mathfrak{s}(T, \rho_1, \ldots, \rho_\mathrm{n})}{\partial \rho_\alpha}$. Here, the spec. entropy is

$$\bar{\mathfrak{s}}_\alpha := \frac{\partial \bar{\mathfrak{s}}}{\partial c_\alpha} = -\frac{\partial^2 \mathfrak{g}}{\partial T \partial c_\alpha} = \bar{\mathfrak{s}}_\alpha(T, p, c_1, \ldots, c_{\mathrm{n}-1}), \tag{2.445}$$

which allows one to write

$$\bar{\mathfrak{h}}_\alpha = \overline{\mu}_\alpha + T \bar{\mathfrak{s}}_\alpha. \tag{2.446}$$

[20] The specific enthalpy was introduced for the variable setting $(T, \rho_1, \ldots, \rho_\mathrm{n})$, however, its definition could straight forward be adopted

Auxiliary calculation 2.36: (Derivation of the heat equation)

$$\begin{aligned}\frac{\partial \rho u}{\partial t} &= (\overline{\mathfrak{g}} - T\frac{\partial \overline{\mathfrak{g}}}{\partial T}) \cdot \frac{\partial n}{\partial t} + n\sum_{\alpha=1}^{\mathrm{n}-1}(\frac{\partial \overline{\mathfrak{g}}}{\partial c_\alpha} - T\frac{\partial^2 \overline{\mathfrak{g}}}{\partial c_\alpha \partial T}) \cdot \frac{\partial c_\alpha}{\partial t} \\ &\quad - T\underbrace{\frac{\partial^2 \overline{\mathfrak{g}}}{\partial^2 T}}_{=:C_T} \cdot \frac{\partial T}{\partial t} - T\underbrace{\frac{\partial^2 \overline{\mathfrak{g}}}{\partial p \partial T}}_{=\kappa_T}\frac{\partial p}{\partial t} \\ &= \sum_{\alpha=1}^{\mathrm{n}} \mathfrak{h}_\alpha \cdot \frac{\partial n_\alpha}{\partial t} - TC_T \cdot \frac{\partial T}{\partial t} - T \cdot \kappa_T \cdot \frac{\partial p}{\partial t}\end{aligned}$$

Inserting the pressure balance

$$\kappa_p \frac{\partial p}{\partial t} = \kappa_T \cdot \frac{\partial T}{\partial t} + \sum_{\alpha=1}^{\mathrm{n}} \kappa_\alpha \frac{\partial n_\alpha}{\partial t}$$

in the internal energy balance leads to

$$\frac{\partial \rho u}{\partial t} = T\sum_{\alpha=1}^{\mathrm{n}}(\frac{\mathfrak{h}_\alpha}{T} - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha)\frac{\partial n_\alpha}{\partial t} - T(C_T + \kappa_p^{-1} \cdot \kappa_T^2) \cdot \frac{\partial T}{\partial t}$$

and finally to the heat equation

$$\begin{aligned}&-(C_T + \kappa_p^{-1} \cdot \kappa_T^2) \cdot \frac{\partial T}{\partial t} \\ &= \frac{1}{T}\frac{\partial \rho u}{\partial t} - \sum_{\alpha=1}^{\mathrm{n}}(\frac{\mathfrak{h}_\alpha}{T} - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha)\frac{\partial n_\alpha}{\partial t} \\ &= \underbrace{\frac{1}{T}\frac{\partial \rho u}{\partial t} - \sum_{\alpha=1}^{\mathrm{n}}\frac{\overline{\mu}_\alpha}{T}\frac{\partial n_\alpha}{\partial t}}_{=-\mathrm{div}\,(n\mathfrak{s}+\bar{\mathbf{j}}_s)+\overline{r}_s} - \sum_{\alpha=1}^{\mathrm{n}}(\overline{\mathfrak{s}}_\alpha - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha)\frac{\partial n_\alpha}{\partial t} \\ &= -\,\mathrm{div}\,(n\mathfrak{s} + \bar{\mathbf{j}}_s) + \sum_{\alpha=1}^{\mathrm{n}} \bar{\mathbf{j}}_\alpha \cdot \left(\nabla\frac{\overline{\mu}_\alpha}{T} - \frac{e_0\, z_\alpha}{T}\mathbf{E}\right) \\ &\qquad - \sum_{\alpha=1}^{\mathrm{n}}\frac{\overline{\mu}_\alpha}{T} \cdot \overline{r}_\alpha + \sum_{\alpha=1}^{\mathrm{n}}(\overline{\mathfrak{s}}_\alpha - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha) \cdot (\mathrm{div}\,(n_\alpha\overline{\mathbf{v}} + \bar{\mathbf{j}}_\alpha) - \overline{r}_\alpha) \\ &= -\mathrm{div}\,(n\mathfrak{s}\mathbf{v} + \bar{\mathbf{j}}_s) + \sum_{\alpha=1}^{\mathrm{n}} \bar{\mathbf{j}}_\alpha^{\mathrm{T}} \cdot \left(\nabla\frac{\overline{\mu}_\alpha}{T} - \frac{e_0\, z_\alpha}{T}\mathbf{E}\right) \\ &\qquad - \sum_{\alpha=1}^{\mathrm{n}}(\frac{\overline{\mathfrak{h}}_\alpha}{T} - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha) \cdot \overline{r}_\alpha + \sum_{\alpha=1}^{\mathrm{n}}(\overline{\mathfrak{s}}_\alpha - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha) \cdot \mathrm{div}\,(n_\alpha\overline{\mathbf{v}} + \bar{\mathbf{j}}_\alpha) \\ &= -\mathrm{div}\left(n\big(\mathfrak{s} - \sum_{\alpha=1}^{\mathrm{n}}(\overline{\mathfrak{s}}_\alpha - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha) \cdot c_\alpha\big)\overline{\mathbf{v}}\right. \\ &\qquad\qquad \left. + \big(\bar{\mathbf{j}}_s - \sum_{\alpha=1}^{\mathrm{n}}(\overline{\mathfrak{s}}_\alpha - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha) \cdot \bar{\mathbf{j}}_\alpha\big)\right) \\ &\qquad + \sum_{\alpha=1}^{\mathrm{n}} \bar{\mathbf{j}}_\alpha^{\mathrm{T}} \cdot \left(\nabla\left(\frac{\overline{\mathfrak{h}}_\alpha}{T} - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha\right) - \frac{e_0\, z_\alpha}{T}\mathbf{E}\right) \\ &\qquad - \sum_{\alpha=1}^{\mathrm{n}}(\frac{\overline{\mathfrak{h}}_\alpha}{T} - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha) \cdot \overline{r}_\alpha - \left(\sum_{\alpha=1}^{\mathrm{n}} n_\alpha \nabla(\overline{\mathfrak{s}}_\alpha - \kappa_T \cdot \kappa_p^{-1} \cdot \kappa_\alpha)\right) \cdot \underline{\overline{\mathbf{v}}^{\mathrm{T}}}\end{aligned}$$

Auxiliary calculation 2.37: (Derivation of the specific enthalpy density)

$$
\begin{aligned}
&(\overline{\mathfrak{g}} - T\frac{\partial\,\overline{\mathfrak{g}}}{\partial\,T})\cdot\frac{\partial\,n}{\partial\,t} + n\sum_{\alpha=1}^{\mathrm{n}-1}\left(\frac{\partial\,\overline{\mathfrak{g}}}{\partial\,c_\alpha} - T\frac{\partial\overline{\mathfrak{g}}}{\partial T\partial c_\alpha}\right)\cdot\frac{\partial\,c_\alpha}{\partial\,t}\\
=&(\overline{\mathfrak{g}} - T\frac{\partial\,\overline{\mathfrak{g}}}{\partial\,T})\cdot\frac{\partial\,n}{\partial\,t} + \sum_{\alpha=1}^{\mathrm{n}-1}\left(\frac{\partial\,\overline{\mathfrak{g}}}{\partial\,c_\alpha} - T\frac{\partial\overline{\mathfrak{g}}}{\partial T\partial c_\alpha}\right)\cdot\left(\frac{\partial\,n_\alpha}{\partial\,t} - c_\alpha\frac{\partial\,n}{\partial\,t}\right)\\
=&\left(\overline{\mathfrak{g}} - T\frac{\partial\,\overline{\mathfrak{g}}}{\partial\,T} - \sum_{\beta=1}^{\mathrm{n}-1}\left(\frac{\partial\,\overline{\mathfrak{g}}}{\partial\,c_\beta} - T\frac{\partial\overline{\mathfrak{g}}}{\partial T\partial c_\beta}\right)c_\beta\right)\cdot\frac{\partial\,n}{\partial\,t} + \sum_{\alpha=1}^{\mathrm{n}-1}\left(\frac{\partial\,\overline{\mathfrak{g}}}{\partial\,c_\alpha} - T\frac{\partial\overline{\mathfrak{g}}}{\partial T\partial c_\alpha}\right)\cdot\frac{\partial\,n_\alpha}{\partial\,t}\\
=&\underbrace{\left(\overline{\mathfrak{g}} - T\frac{\partial\,\overline{\mathfrak{g}}}{\partial\,T} - \sum_{\beta=1}^{\mathrm{n}-1}\left(\frac{\partial\,\overline{\mathfrak{g}}}{\partial\,c_\beta} - T\frac{\partial\overline{\mathfrak{g}}}{\partial T\partial c_\beta}\right)c_\beta\right)}_{=:\mathfrak{h}_\mathrm{n}}\cdot\frac{\partial\,n_\mathrm{n}}{\partial\,t}\\
&+\sum_{\alpha=1}^{\mathrm{n}-1}\underbrace{\left(\overline{\mathfrak{g}} - T\frac{\partial\,\overline{\mathfrak{g}}}{\partial\,T} - \sum_{\beta=1}^{\mathrm{n}-1}\left(\frac{\partial\,\overline{\mathfrak{g}}}{\partial\,c_\beta} - T\frac{\partial\overline{\mathfrak{g}}}{\partial T\partial c_\beta}\right)c_\beta + \frac{\partial\,\overline{\mathfrak{g}}}{\partial\,c_\alpha} - T\frac{\partial\overline{\mathfrak{g}}}{\partial T\partial c_\alpha}\right)}_{=:\mathfrak{h}_\alpha}\cdot\frac{\partial\,n_\alpha}{\partial\,t}
\end{aligned}
$$

2.9 Material functions

In this section the derivation of material functions $\mathfrak{f}$ and $\mathfrak{g}$ is sketched, followed by some explicit representations of $\mathfrak{g}$ for an incompressible liquid and $\mathfrak{f}$ for solid electrolyte.

The derivation is essentially based on integrating the Pfaffian form for g, *i.e.*

$$\int_0^t \frac{\partial \mathfrak{g}}{\partial t} dt = \int_0^t \mathfrak{s} \cdot \frac{\partial T}{\partial t} dt + \int_0^t \overline{v} \cdot \frac{\partial p}{\partial t} dt + \int_0^t \mathfrak{g}_\alpha \cdot \frac{\partial c_\alpha}{\partial t} dt \tag{2.447}$$

$$= \int_{T_0}^{T(t)} \mathfrak{s}(T, p, c_1, \ldots, c_{\mathrm{n}-1}) d\,T + \int_{p_0}^{p(t)} \overline{v}(T, p, c_1, \ldots, c_{\mathrm{n}-1}) d\,p \tag{2.448}$$

$$+ \sum_{\alpha=1}^{\mathrm{n}-1} \int_{c_{\alpha,0}}^{c_\alpha(t)} \mathfrak{g}_\alpha(T, p, c_1, \ldots, c_{\mathrm{n}-1}) d\,c_\alpha. \tag{2.449}$$

However, the material function is restricted by the integrability conditions

$$\frac{\partial}{\partial T}\left(\frac{\partial \mathfrak{g}}{\partial p}\right) = \frac{\partial}{\partial p}\left(\frac{\partial \mathfrak{g}}{\partial T}\right) \tag{2.450}$$

$$\Rightarrow \frac{\partial \overline{v}(T, p, c_1, \ldots, c_{\mathrm{n}-1})}{\partial T} \stackrel{!}{=} \frac{\partial \mathfrak{s}(T, p, c_1, \ldots, c_{\mathrm{n}-1})}{\partial p} \tag{2.451}$$

$$\frac{\partial}{\partial p}\left(\frac{\partial \mathfrak{g}}{\partial c_\alpha}\right) = \frac{\partial}{\partial c_\alpha}\left(\frac{\partial \mathfrak{g}}{\partial p}\right) \tag{2.452}$$

$$\Rightarrow \frac{\partial \mathfrak{g}_\alpha(T, p, c_1, \ldots, c_{\mathrm{n}-1})}{\partial p} \stackrel{!}{=} \frac{\partial \overline{v}(T, p, c_1, \ldots, c_{\mathrm{n}-1})}{\partial c_\alpha} \tag{2.453}$$

$$\frac{\partial}{\partial c_\alpha}\left(\frac{\partial \mathfrak{g}}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial \mathfrak{g}}{\partial c_\alpha}\right) \qquad \alpha = 1, \ldots, \mathrm{n}-1 \tag{2.454}$$

$$\Rightarrow \frac{\partial \mathfrak{s}(T, p, c_1, \ldots, c_{\mathrm{n}-1})}{\partial c_\alpha} \stackrel{!}{=} \frac{\partial \mathfrak{g}_\alpha(T, p, c_1, \ldots, c_{\mathrm{n}-1})}{\partial T} \tag{2.455}$$

$$\frac{\partial}{\partial c_\alpha}\left(\frac{\partial \mathfrak{g}}{\partial c_\beta}\right) = \frac{\partial}{\partial c_\beta}\left(\frac{\partial \mathfrak{g}}{\partial c_\alpha}\right) \qquad \alpha, \beta = 1, \ldots, \mathrm{n}-1 \tag{2.456}$$

$$\Rightarrow \frac{\partial \mathfrak{g}_\alpha(T, p, c_1, \ldots, c_{\mathrm{n}-1})}{\partial c_\beta} = \frac{\partial \mathfrak{g}_\beta(T, p, c_1, \ldots, c_{\mathrm{n}-1})}{\partial c_\alpha}. \tag{2.457}$$

Quite similar, for the free energy $\rho\psi = \mathfrak{f}$ one has the differential form

$$\mathrm{d}\mathfrak{f} = \mathfrak{s}(T, n_1, \ldots, \mathrm{n})\mathrm{d}T + \sum_{\alpha=1}^{\mathrm{n}} \mathfrak{f}_\alpha(T, n_1, \ldots, \mathrm{n})\mathrm{d}n_\alpha \tag{2.458}$$

which imply the integrability conditions

$$\frac{\partial \mathfrak{s}}{\partial n_\alpha} \stackrel{!}{=} \frac{\partial \mathfrak{f}_\alpha}{\partial T} \qquad \alpha = 1, \ldots, \mathrm{n} \tag{2.459}$$

$$\frac{\partial \mathfrak{f}_\alpha}{\partial n_\beta} \stackrel{!}{=} \frac{\partial \mathfrak{f}_\beta}{\partial n_\alpha} \qquad \alpha = 1, \ldots, \mathrm{n}. \tag{2.460}$$

This approach dates back the work of C. Caratheodory [33, 34] at the beginning of the 20th century. I will only give a brief sketch of the derivation for the sake of a motivation with quite restrictive assumptions. Detailed derivations of material functions for mixtures

are given in [25, 27, 35].

One central assumption is the incompressibility $\overline{v} = \text{const.} = n^{-1}$ for the material function $\mathfrak{g}$ and a constant (reference) number density n_n for the free energy. The first implies

$$\frac{\partial \overline{v}}{\partial p} = 0 \qquad \Rightarrow \mathfrak{s} = \mathfrak{s}(T, c_1, \ldots, c_{\text{n}-1}) \tag{2.461}$$

$$\frac{\partial \overline{v}}{\partial c_\alpha} = 0 \qquad \Rightarrow \mathfrak{g}_\alpha = \mathfrak{g}_\alpha(T, c_1, \ldots, c_{\text{n}-1}) \tag{2.462}$$

$$\tag{2.463}$$

and

$$\int_{p_0}^{p(t)} \overline{v} d\, p = (p(t) - p_0) \cdot n^{-1}. \tag{2.464}$$

If n_n is assumed to be fixed, the differential form of $\rho\psi$ is simply

$$\mathrm{d}\mathfrak{f} = \mathfrak{s}(T, n_1, \ldots, n_\text{n})\mathrm{d}T + \sum_{\alpha=1}^{\text{n}-1} \mathfrak{f}_\alpha(T, n_1, \ldots, n_\text{n})\mathrm{d}n_\alpha \tag{2.465}$$

i.e. the nth species does not contribute to the free energy **change**. Nevertheless, $\mathfrak{f}$ is in general a function of n_n (or some variable transformations of n_n).

Next, some common assumptions on the material functions $\mathfrak{s}$ and $\mathfrak{g}_\alpha$ (or $\mathfrak{f}_\alpha$) are given. First, the entropy function $\mathfrak{s}$ is assumed to be decomposed[21] into a configurational contribution $\mathfrak{s}_\text{heat}$ and a heat contribution $\mathfrak{s}_\text{heat}$ with

$$\mathfrak{s}(T, c_1, \ldots, c_{\text{n}-1}) = \mathfrak{s}_\text{conf}(c_1, \ldots, c_{\text{n}-1}) + \mathfrak{s}_\text{heat}(T). \tag{2.466}$$

A common approach for $\mathfrak{s}_\text{heat}(T)$ is $\mathfrak{s}_\text{heat}(T) = C_T \cdot T$ with a constant heat capacity $C_T = \text{const.}$
Second, the partial Gibbs energies $\mathfrak{g}_\alpha$ are assumed to be decomposed as

$$\mathfrak{g}_\alpha = \overline{\mu}_\alpha^\text{R} - T \cdot \mathfrak{s}_\alpha(c_1, \ldots, c_\text{n} - 1) \tag{2.467}$$

where R is some reference state. Note that the integrability condition imply

$$\frac{\partial \mathfrak{s}_\text{conf}}{\partial c_\alpha} \overset{!}{=} \frac{\partial T \cdot \mathfrak{s}_\alpha(c_1, \ldots, c_\text{n} - 1)}{\partial T} = \mathfrak{s}_\alpha(c_1, \ldots, c_{\text{n}-1}) \tag{2.468}$$

in the variable setting $(T, p, c_1, \ldots, c_{\text{n}-1})$.

[21] Note that such decompositions could also be derived via some partial integrations and multi-dimensional integration *constants*.

2.9.1 Configurational entropy

The configurational entropy contribution to explicit material functions are in general derived from statistical mechanics via the well known formula

$$S = k_{\mathrm{B}} \ln (W) \tag{2.469}$$

where W is the amount of microstates a system could capture and k_{B} Boltzmann's constant. Note that statical mechanics essentially derives the microstates as function of atom positions and velocities. Its transition thermodynamic interpretation of **states** as configuration of atoms on a lattice is far more complex, and I refer to standard textbooks for this derivation.

However, assuming that this transition is valid, one could interpret W as the amount of particle configurations, which splits in two groups,

- the configuration of Boson like particles
- and the configuration of Fermion like particles.

The term *like* is used here as boson particles on a lattice, *e.g.* a solid electrolyte or a surface with a finite amount of adsorption sites, behave somehow like fermions, even though the actual atomic particle is a boson.

Configurational entropy of Bosons

Consider N particles, which decompose into a set of n different species, *i.e.*

$$N = \sum_{\alpha=1}^{\mathrm{n}} N_\alpha, \tag{2.470}$$

and are among themselves not distinguishable. Then the number of configurations is then

$$W_B = \binom{N}{N_1, \ldots, N_{\mathrm{n}}} \tag{2.471}$$

where $\binom{N}{N_1,\ldots,N_{\mathrm{n}}}$ denotes the multinomial coefficient

$$\binom{N}{N_1, \ldots, N_{\mathrm{n}}} = \frac{N!}{\prod_{\alpha=1}^{\mathrm{n}} N_\alpha!} \tag{2.472}$$

and for $\mathrm{n} = 2$ simply the binomial coefficient

$$\binom{N}{N_1} = \frac{N!}{N_1! \cdot (N - N_1)!} = \frac{N!}{N_1 \cdot N_2!}. \tag{2.473}$$

Hence, the entropy is simply

$$S = k_{\mathrm{B}} \cdot \ln \left(\frac{N}{N_1, \ldots, N_{\mathrm{n}}} \right) = k_{\mathrm{B}} \cdot \ln (N!) - \sum_{\alpha=1}^{\mathrm{n}} \ln (N_\alpha!) \,. \tag{2.474}$$

If the numbers N_α are quite large (statistical mechanics assumption), it is common to approximate

$$\ln(N_\alpha!) = N_\alpha \ln(N_\alpha) - N_\alpha + \mathcal{O}(\ln(N_\alpha)) \approx N_\alpha \ln(N_\alpha) - N_\alpha \tag{2.475}$$

with Sterlings formula. Hence the entropy is

$$S = k_\mathrm{B} \cdot (N \ln(N) - \sum_{\alpha=1}^{\mathrm{n}} N_\alpha \ln(N_\alpha)) = -k_\mathrm{B} \sum_{\alpha=1}^{\mathrm{n}} N_\alpha \ln\left(\frac{N_\alpha}{N}\right). \tag{2.476}$$

The transition to a local formulation of the configurational entropy is employed with a continuum hypothesis, *i.e.* the assumption that the density formulation

$$n\mathfrak{s}_\mathrm{conf} = -k_\mathrm{B} \sum_{\alpha=1}^{\mathrm{n}} n_\alpha \ln\left(\frac{n_\alpha}{n}\right) \tag{2.477}$$

$$= -n\, k_\mathrm{B} \sum_{\alpha=1}^{\mathrm{n}} c_\alpha \ln(c_\alpha) \tag{2.478}$$

$$= -n\, k_\mathrm{B} \left(\sum_{\alpha=1}^{\mathrm{n}-1} c_\alpha \ln\left(\frac{c_\alpha}{1-\sum_{\beta=1}^{\mathrm{n}-1} c_\beta}\right) + \ln\left(1 - \sum_{\beta=1}^{\mathrm{n}-1} c_\beta\right)\right) \tag{2.479}$$

holds. The integrability condition (2.468) implies

$$\mathfrak{s}_\alpha(c_1, \ldots, c_{\mathrm{n}-1}) = k_\mathrm{B} \cdot \ln\left(\frac{c_\alpha}{1-\sum_{\beta=1}^{\mathrm{n}} c_\beta}\right). \tag{2.480}$$

Auxiliary calculation 2.38:

Using the relation $c_\mathrm{n} = 1 - \sum_{\beta=1}^{\mathrm{n}-1} c_\beta$ leads to

$$\frac{\partial\, \mathfrak{s}_\mathrm{conf}}{\partial\, c_\gamma} = \sum_{\alpha=1}^{\mathrm{n}-1} \left(\delta_{\alpha,\gamma} \cdot \ln\left(\frac{c_\alpha}{1-\sum_{\beta=1}^{\mathrm{n}-1} c_\beta}\right) + c_\alpha \frac{c_\mathrm{n}}{c_\alpha} \cdot \left(\frac{\delta_{\alpha,\beta}}{c_\mathrm{n}} - \frac{c_\alpha}{c_\mathrm{n}}\right)\right) - \frac{1}{c_n}$$

$$= \ln\left(\frac{c_\gamma}{1-\sum_{\beta=1}^{\mathrm{n}-1} c_\beta}\right) + \sum_{\alpha=1}^{\mathrm{n}-1} \left(\delta_{\alpha,\gamma} - \frac{c_\alpha}{c_\mathrm{n}}\right) - \frac{1}{c_\mathrm{n}} = \ln\left(\frac{c_\gamma}{c_\mathrm{n}}\right)$$

Configurational entropy on latices

In the above derived configurational entropy it was essentially assumed that the each *site* or *allowed position* in space is occupied by one of the particles. In contrast, distributing the $N_1, \ldots, N_{\mathrm{n}-1}$ particles on a lattice with N_ℓ sites leads to the amount of possible configurations

$$W = \binom{N_\ell}{N_1, \ldots, N_{\mathrm{n}-1}, (N_\ell - \sum_{\alpha=1}^{\mathrm{n}-1} N_\alpha)}. \tag{2.481}$$

Introducing the number of vacancies as

$$N_v = N_\ell - \sum_{\alpha=1}^{\mathrm{n}-1} N_\alpha, \tag{2.482}$$

and applying the Sterlings formula leads to the configurational entropy function

$$S = k_{\mathrm{B}} \cdot (N_\ell \cdot \ln(N_\ell) - N_\ell - \sum_{\alpha=1}^{\mathrm{n}-1} N_\alpha \cdot \ln(N_\alpha) + \sum_{\alpha=1}^{\mathrm{n}-1} N_\alpha) - N_v \cdot \ln(N_v) + N_v \tag{2.483}$$

$$= -k_{\mathrm{B}} \left(N_v \cdot \ln\left(\frac{N_v}{N_\ell}\right) + \sum_{\alpha=1}^{\mathrm{n}-1} N_\alpha \cdot \ln\left(\frac{N_\alpha}{N_\ell}\right) \right). \tag{2.484}$$

Note that *only* $(\mathrm{n}-1)$ distinguishable species are are placed on the lattice, as the lattice itself is *built* by the nth species ($N_\ell = N_\ell(N_{\mathrm{n}})$). The explicit dependency of N_ℓ is derived below. Introducing the **site density** n_ℓ via

$$N_\ell = \int_\Omega n_\ell(\mathbf{y}, t)\, dV \tag{2.485}$$

and consequently the **vacancies density** n_v as

$$n_v(\mathbf{y}, t) := n_\ell(\mathbf{y}, t) - \sum_{\alpha=1}^{\mathrm{n}-1} \tag{2.486}$$

$$N_v = \int_\Omega n_v(\mathbf{y}, t)\, dV \tag{2.487}$$

leads to the configurational entropy density

$$\mathfrak{s}_{\mathrm{conf}} = -k_{\mathrm{B}} \cdot (n_v \ln\left(\frac{n_v}{n_\ell}\right) + \sum_{\alpha=1}^{\mathrm{n}-1} n_\alpha \ln\left(\frac{n_\alpha}{n_\ell}\right)). \tag{2.488}$$

On a lattice it is thus quite convenient to introduce the **coverage**[22] θ_α of species α as

$$\theta_\alpha := \frac{n_\alpha}{n_\ell} \qquad \alpha = 1, \ldots, \mathrm{n}-1 \tag{2.489}$$

$$\theta_v := \frac{n_v}{n_\ell} \tag{2.490}$$

with

$$\sum_{\alpha=1}^{\mathrm{n}-1} \theta_\alpha + \theta_v = 1 \tag{2.491}$$

Sometimes the coverage is then interpreted as *concentration* and the *natural* variables on a lattice the are $(T, n_\ell, \theta_1, \ldots, \theta_{\mathrm{n}-1})$.

Due to the introduction of the lattice sites n_ℓ as independent degree of freedom, n_{n} is a derived property, *i.e.*

$$n_{\mathrm{n}} = n_{\mathrm{n}}(T, n_\ell, \theta_1, \ldots, \theta_{\mathrm{n}-1}), \tag{2.492}$$

which of course has some major consequences. However, I will assume in the further work a simple relationship

$$n_{\mathrm{n}} = \kappa_\ell \cdot n_\ell \tag{2.493}$$

[22]Note that coverage does not mean here coverage of a surface, but volumetric coverage.

as more general relationships are subject current and further work.

Remark 9 (Chemical potential on a lattice).

The chemical potential per particle $\overline{\mu}_\alpha$ in the variable setting $(T, n_1, \ldots, n_\mathrm{n})$ is obtained from the free energy density $\mathfrak{f}(T, n_1, \ldots, n_\mathrm{n}) = \rho\psi$ as

$$\overline{\mu}_\alpha = \frac{\partial \mathfrak{f}}{\partial n_\alpha},$$

which follows directly from the definition of μ_α and $\overline{\mu}_\alpha$. Performing the variable change $(n_1, \ldots, n_\mathrm{n}) \to (n_\ell, \theta_1, \ldots, \theta_{\mathrm{n}-1})$, *i.e.*

$$\mathfrak{f} = \mathfrak{f}(T, n_\ell \cdot \theta_1, \ldots, n_\ell \cdot \theta_{\mathrm{n}-1}, \kappa_\ell \cdot n_\ell) =: \hat{\mathfrak{f}}(T, n_\ell, \theta_1, \ldots, \theta_{\mathrm{n}-1}) \tag{2.494}$$

implies

$$\overline{\mu}_\alpha = n_\ell^{-1} \cdot \frac{\partial \hat{\mathfrak{f}}}{\partial \theta_\alpha} = \overline{\mu}_\alpha(T, n_\ell, \theta_1, \ldots, \theta_{\mathrm{n}-1}) \qquad \alpha = 1, \ldots, \mathrm{n}-1 \tag{2.495}$$

$$\overline{\mu}_\mathrm{n} = \kappa_\ell^{-1} \cdot \left(\frac{\partial \hat{\mathfrak{f}}}{\partial n_\ell} - n_\ell^{-1} \sum_{\alpha=1}^{\mathrm{n}-1} \frac{\partial \hat{\mathfrak{f}}}{\partial \theta_\alpha} \right) = \overline{\mu}_\mathrm{n}(T, n_\ell, \theta_1, \ldots, \theta_{\mathrm{n}-1}). \tag{2.496}$$

The chemical potential $\overline{\mu}_\alpha$ of species α in the variable setting $(T, n_\ell, \theta_1, \ldots, \theta_{\mathrm{n}-1})$ is further called **chemical potential on a lattice**.

Auxiliary calculation 2.39:

$$\frac{\partial \hat{\mathfrak{f}}}{\partial \theta_\alpha} = \frac{\partial \mathfrak{f}}{\partial n_\alpha} \cdot n_\ell$$

$$\frac{\partial \hat{\mathfrak{f}}}{\partial n_\ell} = \sum_{\alpha=1}^{\mathrm{n}-1} \frac{\partial \mathfrak{f}}{\partial n_\alpha} \cdot \theta_\alpha + \frac{\partial \mathfrak{f}}{\partial n_\mathrm{n}} \cdot \kappa_\ell = \sum_{\alpha=1}^{\mathrm{n}-1} \overline{\mu}_\alpha \theta_\alpha + \kappa_\alpha \cdot \overline{\mu}_\mathrm{n}$$

Remark 10 (Frame of reference on a lattice structure).

Let n_ℓ be the total number density of lattice sites with

$$N_\ell = \int_\Omega n_\ell \, dV \tag{2.497}$$

and

$$\frac{\mathrm{d} N_\ell}{\mathrm{d} t} = \int_{\partial\Omega} \hat{\mathbf{j}}_\ell \cdot \, d\mathbf{A} + \int_\Omega \hat{r} \, dV \tag{2.498}$$

where

- $\hat{\mathbf{j}}_\ell$ is the diffusive *flux* of lattice sites
- and $\hat{r}$ is the source or sink of lattice sites.

Choosing a frame of reference $(\boldsymbol{\xi}, \hat{\mathbf{v}}), \boldsymbol{\xi} \in \Omega$ such that

$$\hat{\mathbf{j}}_\ell(\boldsymbol{\xi}, t) = \mathbf{0} \tag{2.499}$$

leads to the balance equation

$$\frac{\partial\, n_\ell}{\partial\, t} = -\mathrm{div}\,(n_\ell \hat{\mathbf{v}}) + \hat{r}_\ell. \tag{2.500}$$

A common **assumption on the of lattice sites** is clearly

$$n_\ell = \text{const.} \qquad \forall(\boldsymbol{\xi}, t) \in \Omega \times I \tag{2.501}$$

$$\hat{r}_\ell = 0 \tag{2.502}$$

which leads to

$$0 = -\mathrm{div}\,(n_\ell \hat{\mathbf{v}}) = -n_\ell \mathrm{div}\,\hat{\mathbf{v}}. \tag{2.503}$$

If the whole domain Ω is assumed to remain fixed in time, *i.e.*

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Omega} 1\, dV = \int\limits_{\partial\Omega} \hat{\mathbf{v}} \cdot\, d\mathbf{A} = 0 \tag{2.504}$$

one obtains[23]

$$\hat{\mathbf{v}}(\boldsymbol{\xi}, t) = \mathbf{0}. \tag{2.506}$$

Hence, the species balance equations in the coordinate system $(\boldsymbol{\xi}, \hat{\mathbf{v}} = \mathbf{0})$ are

$$n_\ell \frac{\partial\, \theta_\alpha(\boldsymbol{\xi}, t)}{\partial\, t} = \frac{\partial\, n_\alpha(\boldsymbol{\xi}, t)}{\partial\, t} = -\mathrm{div}\,\hat{\mathbf{j}}_\alpha(\boldsymbol{\xi}, t) + \hat{r}_\alpha(\boldsymbol{\xi}, t). \tag{2.507}$$

The relation $n_\ell = \kappa_\ell \cdot n_\mathrm{n}$, together with the assumption $n_\ell = \text{const.}$ and the coordinate system choice $(\boldsymbol{\xi}, \hat{\mathbf{v}} = \mathbf{0})$ implies $\mathbf{j}_\mathrm{n} = \mathbf{0}$ (which follows from a comparison of the balance equations for n_ℓ and n_n). Hence, the flux entropy production is simply[24]

$$\hat{r}_{s,\mathbf{j}} = \hat{\mathbf{j}}_u^\mathrm{T} \cdot \underbrace{\nabla \frac{1}{T}}_{=:\gamma_0} + \sum_{\alpha=1}^{\mathrm{n}-1} \hat{\mathbf{j}}_\alpha^\mathrm{T} \cdot \underbrace{\left(\nabla \frac{\overline{\mu}_\alpha}{T} - \frac{e_0 z_\alpha}{T}\mathbf{E}\right)}_{=:\hat{\gamma}_\alpha} \tag{2.509}$$

[23]This could have also been derived in the very beginning of the derivation, stating $n_\ell = \text{const.}$ and $\Omega = \text{const.}$ which leads to

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\limits_{\Omega} n_\ell\, dV = \int\limits_{\Omega} \frac{\partial\, n_\ell}{\partial\, t}\, dV \overset{!}{=} \oint\limits_{\partial\Omega} \hat{\mathbf{j}}_\ell\, d\mathbf{A} \qquad \Rightarrow \qquad \frac{\partial\, n_\ell}{\partial\, t} = -\mathrm{div}\,\hat{\mathbf{j}}_\ell.$$

Yet, the coordinate system is arbitrary and $(\boldsymbol{\xi}, \hat{\mathbf{v}})$ is chosen such that $\hat{\mathbf{j}}_\ell(\boldsymbol{\xi}, t) = \mathbf{0}$, which implies $\hat{\mathbf{v}} = \mathbf{0}$. Hence, the balance equation of n_ℓ,

$$\underbrace{\frac{\partial\, n_\ell}{\partial\, t}}_{=0} = -\mathrm{div}\, \underbrace{\hat{\mathbf{j}}_\ell}_{=\mathbf{0}}, \tag{2.505}$$

is trivially satisfied and, and the coordinate system $(\boldsymbol{\xi}, \hat{\mathbf{v}} = \mathbf{0})$ is chosen for the species balance equation.

[24]In the general case, with $(\mathbf{x}, \mathbf{v})$ as coordinate system, the flux constraint $\sum_{\alpha=1}^{\mathrm{n}} \mathbf{j}_\alpha = \mathbf{0}$ implies

$$\mathbf{j}_\alpha \propto \nabla \frac{\mu_\alpha - \mu_\mathrm{n}}{T} - \frac{e_0}{T}\left(\frac{z_\alpha}{m_\alpha} - \frac{z_\mathrm{n}}{m_\mathrm{n}}\right) \qquad \alpha = 1, \ldots, \mathrm{n}-1. \tag{2.508}$$

Here, however, due to the constraint $\hat{\mathbf{j}}_\mathrm{n} = \mathbf{0}$, thermodynamic part of the driving force is *only* $\overline{\mu}_\alpha$, and not the difference $\overline{\mu}_\alpha - \overline{\mu}_\mathrm{n}$.

and the entropy principle leads to the choice

$$\hat{\underline{\mathbf{j}}} = \hat{\underline{\underline{\mathbf{L}}}} \cdot \hat{\underline{\gamma}} \tag{2.510}$$

with a positive definite, symmetric *matrix* $\hat{\underline{\underline{\mathbf{L}}}}$. The symmetry of $\hat{\underline{\underline{\mathbf{L}}}}$ is again a consequence of assumption 16 and theorem 9.

The representation of the configurational entropy on a lattice is

$$\mathfrak{s}_{\mathrm{conf}}(n_\ell, \theta_1, \ldots, \theta_{\mathrm{n}-1}) = -n_\ell k_{\mathrm{B}} \cdot (\theta_V \ln(\theta_V) + \sum_{\alpha=1}^{\mathrm{n}} \theta_\alpha \ln(\theta_\alpha)). \tag{2.511}$$

Due to the variable change $(T, n_1, \ldots, n_{\mathrm{n}}) \to (T, n_\ell, \theta_1, \ldots, \theta_{\mathrm{n}-1})$, the integrability condition for the configuration $\mathfrak{s}_{\mathrm{conf}}$ entropy and partial entropy $\mathfrak{s}_\alpha$ reads

$$\frac{\partial \mathfrak{s}_{\mathrm{conf}}}{\partial n_\alpha} = n_\ell^{-1} \frac{\partial \mathfrak{s}_{\mathrm{conf}}}{\partial \theta_\alpha} \stackrel{!}{=} \mathfrak{s}_\alpha(\theta_1, \ldots, \theta_{\mathrm{n}-1}) \qquad \alpha = 1, \ldots, \mathrm{n}-1 \tag{2.512}$$

and thus

$$\mathfrak{s}_\alpha(\theta_1, \ldots, \theta_{\mathrm{n}-1}) = -k_{\mathrm{B}} \ln\left(\frac{\theta_\alpha}{\theta_V}\right). \tag{2.513}$$

2.9.2 Polarization effects

Polarization and magnetization arises in the entropy function according to Gibbs equation

$$\rho\psi + p + \frac{1}{2}\varepsilon_0^{-1}\mathbf{D} \cdot \mathbf{P}^{\mathrm{T}} - \frac{1}{2}\mathbf{B} \cdot \mathbf{M}^{\mathrm{T}} = \sum_{\alpha=1}^{\mathrm{n}} \mu_\alpha \cdot \rho_\alpha. \tag{2.514}$$

Throughout the rest of the work, magnetic contributions are neglected, as the whole electrolytic theory including magnetic (and thus inductive) effects is current research work.

It is further assumed that Polarization is just simply related (*c.f.* remark 5) to the electric flux density via[36]

$$\mathbf{P} = \chi^P \mathbf{D} \tag{2.515}$$

where $\chi^P = \mathrm{const}$. For a mixture (*c.f.* eq. 2.93), however, a polarization model

$$\mathbf{P} = \varepsilon_0 \left(\sum_{\alpha=1}^{\mathrm{n}} c_\alpha(\mathbf{x}, t)\chi_\alpha^P\right) \mathbf{D} \tag{2.516}$$

is more appropriate, however, it is fairly assumed that

$$\mathbf{P} = \chi_{\mathrm{n}}^P \mathbf{D}, \tag{2.517}$$

where χ_{n}^P is the permittivity of the solvent, is quite a good approximation.

If $\mathfrak{f}$ is the free energy without polarization one uses thus

$$\mathfrak{f}^P = \mathfrak{f} + \chi_{\mathrm{n}}^P \varepsilon_0^{-1} \mathbf{D} \cdot \mathbf{D}^{\mathrm{T}} \tag{2.518}$$

as material function for the free energy. The transition to the Gibbs energy (per particles)

including polarization effects is simply

$$\mathfrak{g}^P = \mathfrak{g} + n^{-1} \cdot \chi_{\mathrm{n}}^P \, \varepsilon_0^{-1} \mathbf{D} \cdot \mathbf{D}^{\mathrm{T}}. \tag{2.519}$$

2.9.3 Additional free energy contributions

A variety of additional contributions to either $\rho\psi$ or g could arise, *e.g.* phase boundaries within Ω, a non-ideal mixing behavior, or additional electrostatic like the Debye–Hückel effect[37]. Contributions due to of a non-ideal mixing behavior are in general modeled via

- a regular solution model [29] or extensions[38],
- activity coefficients γ_i, [39–41],
- or any other excess contributions $g_{\mathbf{chem}}^{\mathrm{ex}}$ (e.g. phase boundaries[42, 43]).

Such activity coefficients could either be constant, $\gamma_i \equiv const.$, space/time dependent, $\gamma_i = \gamma_i(\mathbf{x}, t)$ or dependent on the actual species density, $\gamma_i = \gamma_i(n_i)$[44]. However, a consistent incorporation of Debye–Hückel theory as well as phase separation in electrolytic materials is subject to recent research work.

2.10 Explicit material functions

2.10.1 Incompressible liquid electrolyte

An incompressible liquid electrolyte (*i.e.* with a constant total number density n) would hence be modeled as a bosonic mixture of n species, where the (uncharged) solvent is classically denoted as the nth species. Its Gibbs free energy material function is hence

$$\mathfrak{g}(T, p, c_1, \ldots, c_{\mathrm{n}-1}) = \sum_{\alpha=1}^{\mathrm{n}} \overline{\mu}_\alpha^{\mathrm{R}} \cdot c_\alpha + T^2 \cdot C_T + n^{-1} \cdot p + k_{\mathrm{B}} T \sum_{\alpha=1}^{\mathrm{n}} c_\alpha \ln(c_\alpha) + \chi_{\mathrm{n}}^P \, \varepsilon_0^{-1} \mathbf{D} \cdot \mathbf{D}^{\mathrm{T}} \tag{2.520}$$

leading to chemical potential

$$\overline{\mu}_\alpha(T, p, c_\alpha) = \overline{\mu}_\alpha^{\mathrm{R}} + n^{-1} \cdot p + k_{\mathrm{B}} T \cdot \ln(c_\alpha) \tag{2.521}$$

Note that $\overline{\mu}_\alpha$ is only dependent on (T, p, c_α). Mixtures of this type are called **ideal mixtures** [5]. Further, even though the mixture is incompressible and liquid, the actual pressure $p(\mathbf{y}, t)$ is present in the chemical potential. In an electrolyte mixture the pressure, however, is not constant throughout the domain (*i.e.* in the space charge regions), and thus the pressure indeed contributes to the flux equilibrium[36]. However, the flux equilibrium in the isothermal case

$$\nabla(\overline{\mu}_\alpha - \overline{\mu}_{\mathrm{n}}) - e_0 z_\alpha \mathbf{E} = \mathbf{0} \tag{2.522}$$

$$\tag{2.523}$$

is independent of the actual pressure, and thus **decouples** from the momentum balance.

If the chemical potentials differences $\overline{\mu}_\alpha - \overline{\mu}_\mathrm{n}$ at a point $\mathbf{x}_A$ in space are known (measured), *i.e.*

$$\overline{\mu}_\alpha(\mathbf{x}_A) - \overline{\mu}_\mathrm{n}(\mathbf{x}_A) = \overline{\mu}_\alpha^\mathrm{R} - \overline{\mu}_\mathrm{n}^\mathrm{R} + k_\mathrm{B} T \ln\left(\frac{c_\alpha^\mathrm{R}}{c_\mathrm{n}^\mathrm{R}}\right) \tag{2.524}$$

one could calculate the equilibrium concentrations c_α at a point $\mathbf{x}$ in space via a path integral of a curve Ψ with starting point $\mathbf{x}_A$ and endpoint $\mathbf{x}$. Since $\mathbf{E}$ is conservative with potential Φ, at least in the quasi-electrostatic case, the electrostatic potential difference between $\mathbf{x}_A$ and $\mathbf{x}$ is

$$\int\limits_\Psi \mathbf{E}\, d\mathbf{s} = \Phi(\mathbf{x}_A) - \Phi(\mathbf{x}) := U_A(\mathbf{x}), \tag{2.525}$$

one obtains the compact relation

$$U_A(\mathbf{x}) = \frac{1}{e_0 z_\alpha}(\overline{\mu}_\alpha(\mathbf{x}_A) - \overline{\mu}_\alpha(\mathbf{x}) - \overline{\mu}_\mathrm{n}(\mathbf{x}_A) + \overline{\mu}_\mathrm{n}(\mathbf{x})) \tag{2.526}$$

$$\Leftrightarrow \qquad c_\alpha(\mathbf{x}) = c_\mathrm{n} \frac{c_\alpha^\mathrm{R}}{c_\mathrm{n}^\mathrm{R}} \cdot \mathrm{e}^{\frac{e_0 z_\alpha}{k_\mathrm{B} T} U_A(\mathbf{x})} \tag{2.527}$$

for $\alpha = 1, \ldots, \mathrm{n}-1$. With the condition

$$\sum_{\alpha=1}^{\mathrm{n}-1} c_\alpha(\mathbf{x}) = 1 - c_\mathrm{n} \tag{2.528}$$

one thus computes $c_\mathrm{n}(\mathbf{x})$ as

$$c_\mathrm{n}(\mathbf{x}) = \frac{1}{1 + \sum_{\beta=1}^{\mathrm{n}-1} \frac{c_\beta^\mathrm{R}}{c_\mathrm{n}^\mathrm{R}} \cdot \mathrm{e}^{\frac{e_0 z_\beta}{k_\mathrm{B} T} U_A(\mathbf{x})}} \tag{2.529}$$

and obtains finally

$$c_\alpha(\mathbf{x}) = \frac{c_\alpha^\mathrm{R} \cdot \mathrm{e}^{\frac{e_0 z_\alpha}{k_\mathrm{B} T} U_A(\mathbf{x})}}{c_\mathrm{n}^\mathrm{R} + \sum_{\beta=1}^{\mathrm{n}-1} c_\beta^\mathrm{R} \cdot \mathrm{e}^{\frac{e_0 z_\beta}{k_\mathrm{B} T} U_A(\mathbf{x})}} \tag{2.530}$$

$$= \frac{c_\alpha^\mathrm{R} \cdot \mathrm{e}^{\frac{e_0 z_\alpha}{k_\mathrm{B} T} U_A(\mathbf{x})}}{1 - \sum_{\beta=1}^{\mathrm{n}-1} c_\beta^\mathrm{R} \cdot (1 - \mathrm{e}^{\frac{e_0 z_\beta}{k_\mathrm{B} T} U_A(\mathbf{x})})} \qquad \alpha = 1, \ldots, \mathrm{n}-1. \tag{2.531}$$

Recall the free charge density

$$n^\mathrm{F}(\mathbf{x}) = n \cdot \sum_{\alpha=1}^{\mathrm{n}} e_0 z_\alpha c_\alpha(\mathbf{x}) \tag{2.532}$$

and the Poisson equation for a simple polarizable material, *i.e.* $\mathbf{P} = \chi \mathbf{D}$, $\chi = \text{const.}$

$$\varepsilon_0 (1 + \chi) \operatorname{div} \nabla \Phi = n^\mathrm{F}. \tag{2.533}$$

Inserting the representation eq. (2.530) for c_α (and $z_\mathrm{n} = 0$) leads to

$$\varepsilon_0(1+\chi)\,\mathrm{div}\,\nabla\Phi = n\cdot e_0 \frac{\sum_{\alpha=1}^{\mathrm{n}-1} z_\alpha \cdot c_\alpha^\mathrm{R} \cdot \mathrm{e}^{\frac{e_0 z_\alpha}{k_\mathrm{B}T} U_A(\mathbf{x})}}{1-\sum_{\beta=1}^{\mathrm{n}-1} c_\beta^\mathrm{R} \cdot (1-\mathrm{e}^{\frac{e_0 z_\beta}{k_\mathrm{B}T} U_A(\mathbf{x})})}. \tag{2.534}$$

This equation is the Poisson–Boltzmann analogy of an **incompressible** electrolyte, and the transient behavior is governed by a *modified* Poisson–Nernst–Planck equation system (*c.f.* section 3.2 and [44]). Note there is a longstanding discussion in literature[36, 45–48] of the actual **shape** of the general Poisson–Boltzmann[25] in an incompressible electrolyte. Quite a similar equation is derived for solid electrolyte, where the rigid lattice is the analogy to the incompressibility. It is further to note that almost ever since in electrochemistry the simplified Poisson–Boltzmann equation

$$\varepsilon_0(1+\chi_\mathrm{n}^P)\,\mathrm{div}\,\nabla\Phi = n\cdot e_0 \sum_{\alpha=1}^{\mathrm{n}-1} z_\alpha \cdot c_\alpha^\mathrm{R} \cdot \mathrm{e}^{\frac{e_0 z_\alpha}{k_\mathrm{B}T} U_A(\mathbf{x})} \tag{2.535}$$

is used to derive model conceptions, such as the Gouy–Chapman model and its extensions. However, its full exploitation and application to basic electrochemical measurements is subject to current research work [49].

2.10.2 Solid electrolyte

A solid electrolyte is described as a mixture of $\mathrm{n}-1$ species on a lattice with constant site density n_ℓ. The configurational entropy is thus of fermionic type, and the corresponding free energy density on a rigid lattice is

$$\begin{aligned}\rho\psi = \mathfrak{f}(T,\theta_1,\ldots,\theta_{\mathrm{n}-1}) = n_\ell \sum_{\alpha=1}^{\mathrm{n}-1} \psi_\alpha^\mathrm{R}\theta_\alpha + n_\ell \sum_{\alpha=1}^{\mathrm{n}-1} k_\mathrm{B}T \cdot \theta_\alpha \cdot \ln\left(\frac{\theta_\alpha}{\theta_V}\right)\\ + n_\ell T^2 \cdot C_T + \chi_\mathrm{n}^P\,\varepsilon_0^{-1}\mathbf{D}\cdot\mathbf{D}^\mathrm{T}\end{aligned} \tag{2.536}$$

leading to the chemical potential

$$\overline{\mu}_\alpha(T,\theta_1,\ldots,\theta_{\mathrm{n}-1}) = \psi_\alpha^\mathrm{R} + k_\mathrm{B}T\ln\left(\frac{\theta_\alpha}{\theta_V}\right) \tag{2.537}$$

and

$$\overline{\mu}_\mathrm{n} = \psi_\mathrm{n} = \mathrm{const.}. \tag{2.538}$$

On page 123 it was shown that the actual driving force of a flux on a lattice

$$\nabla\frac{\overline{\mu}_\alpha}{T} - \frac{e_0\,z_\alpha}{T}\mathbf{E}. \tag{2.539}$$

In flux equilibrium one could thus again integrate the condition

$$\nabla\frac{\overline{\mu}_\alpha}{T} - \frac{e_0\,z_\alpha}{T}\mathbf{E} \overset{!}{=} \mathbf{0} \tag{2.540}$$

[25] The term Boltzmann is historically used as the first type this equation was derived from statistical mechanics with a Boltzmann distribution for the species densities.

via a path integral of a curve Ψ ranging from $\mathbf{x}_A$ to a point $\mathbf{x}$ in space. In the electrostatic limit, $\mathbf{E}$ is again conservative with potential Φ, allowing thus a direct evaluation of

$$\int_{\Psi} \nabla \frac{\overline{\mu}_\alpha}{T} - \frac{e_0\, z_\alpha}{T} \nabla \Phi \, d\mathbf{s} = 0 \tag{2.541}$$

and consequently

$$\overline{\mu}_\alpha(\mathbf{x}) - \overline{\mu}_\alpha(\mathbf{x}_A) = e_0 z_\alpha U_A(\mathbf{x}). \tag{2.542}$$

If the concentrations or coverages at $\mathbf{x}_A$ are simply $\theta_\alpha^{\mathrm{R}}$, one obtains the representation

$$\theta_\alpha = \theta_V \cdot \frac{\theta_\alpha^{\mathrm{R}}}{\theta_V^{\mathrm{R}}} \cdot \mathrm{e}^{\frac{e_0\, z_\alpha}{k_{\mathrm{B}} T} U_A(\mathbf{x})} \tag{2.543}$$

and with AC 2.40 finally

$$\theta_\alpha(\mathbf{x}) = \frac{\theta_\alpha^{\mathrm{R}} \cdot \mathrm{e}^{\frac{e_0\, z_\alpha}{k_{\mathrm{B}} T} U_A(\mathbf{x})}}{\theta_V^{\mathrm{R}} + \sum_{\beta=1}^{\mathrm{n}-1} \theta_\beta^{\mathrm{R}} \cdot \mathrm{e}^{\frac{e_0\, z_\beta}{k_{\mathrm{B}} T} . U_A(\mathbf{x})}} \tag{2.544}$$

Note that this representation of the *coverage* or concentration on a rigid volumetric lattice is quite similar to the representation of the concentration in an incompressible liquid.

Auxiliary calculation 2.40:

$$\sum_{\alpha=1}^{\mathrm{n}-1} \theta_\alpha = \sum_{\alpha=1}^{\mathrm{n}-1} \theta_V \cdot \frac{\theta_\alpha^{\mathrm{R}}}{\theta_V^{\mathrm{R}}} \cdot \mathrm{e}^{\frac{e_0\, z_\alpha}{k_{\mathrm{B}} T} U_A(\mathbf{x})} = 1 - \theta_V$$

$$\Rightarrow \theta_V = \frac{1}{1 + \sum_{\alpha=1}^{\mathrm{n}-1} \frac{\theta_\alpha^{\mathrm{R}}}{\theta_V^{\mathrm{R}}} \cdot \mathrm{e}^{\frac{e_0\, z_\alpha}{k_{\mathrm{B}} T} U_A(\mathbf{x})}}$$

The representation of the free charge density within a solid electrolyte is

$$n^{\mathrm{F}} = e_0 \sum_{\alpha=1}^{\mathrm{n}} z_\alpha n_\alpha \tag{2.545}$$

$$= n_\ell \cdot e_0 \sum_{\alpha=1}^{\mathrm{n}-1} z_\alpha \theta_\alpha + e_0 z_{\mathrm{n}} \kappa_\ell \cdot n_\ell \tag{2.546}$$

and z_{n} is general **not** zero[26]. Inserting eqs. (2.544) with (2.545) in the Poisson equation (with a simple polarization model) one obtains the **generalized Poisson–Boltzmann equation for solid electrolytes** [50]

$$\varepsilon_0 (1 + \chi_{\mathrm{n}}^P) \mathrm{div}\, \nabla \Phi = n_\ell\, e_0 \cdot \left(\frac{\sum_{\alpha=1}^{\mathrm{n}-1} z_\alpha\, \theta_\alpha^{\mathrm{R}} \cdot \mathrm{e}^{\frac{e_0\, z_\alpha}{k_{\mathrm{B}} T} U_A(\mathbf{x})}}{\theta_V^{\mathrm{R}} + \sum_{\beta=1}^{\mathrm{n}-1} \theta_\beta^{\mathrm{R}} \cdot \mathrm{e}^{\frac{e_0\, z_\beta}{k_{\mathrm{B}} T} U_A(\mathbf{x})}} + z_{\mathrm{n}} \cdot \kappa_\ell \right). \tag{2.547}$$

[26] The species n or equivalent, the lattice, is itself charged as it represents the anionic background *jelly* or charge density to establish electroneutrality in the bulk.

3

Mathematical Modeling of Lithium Ion Batteries

This section covers some parts and figures of the published article

> M. Landstorfer and T. Jacob, Mathematical modeling of intercalation batteries at the cell level and beyond, *Chem. Soc. Rev.*, 2013, **42**, 3234–3252, (`http://pubs.rsc.org/en/content/articlelanding/2013/cs/c2cs35050e/`)

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3.1 Introduction

Mathematical modeling of batteries attempts to describe the electrochemical system in terms of balance equations covering some constitutive parameters, with the purpose of predicting the system behavior. Necessity could arise because an experimental or metrological access is only partly possible or even impossible, time consuming, or too expensive. Classical questions in battery modeling are for example

- How and why does the cell potential vary during operation?
- How much heat is generated or dissipated during charging or discharging?
- Why and how do battery cells degrade and how to estimate the lifetime and cycling stability?

For predictive purpose of mathematical modeling, a self consistent based derivation of the balance equations based on coupled thermo- and electrodynamics is necessary in order to account for the various effects which occur in this highly complex system

However, dependent on the application of a mathematical model, the level of accuracy, and thus of complexity, has to be chosen appropriately. In electronic engineering the question *why* an electrochemical reaction occurs is usually not the main focus, as long as the equivalent circuit model of the battery is valid. Contrary, in computer aided search and development of new materials this question is crucial. Hence a natural clustering of the addressed issues in terms of time- and length scales is possible, but certainly not unique. Growing computer power as well as sophisticated method developments led to an

overlap between these clusters and smeared the boarders between physics, chemistry and adjacent disciplines. This somehow motivates a careful reformulation of various questions in battery modeling.[44] In that sense, this work has to be understood as a very basis of consistent modeling approach, allowing for successive simplification due classical assumptions, asymptotic calculus or homogenization techniques.

3.1.1 Brief historic overview

Modeling of battery systems began around 1970 with the mathematical treatment of porous electrodes and the derivation of *averaged* flux and reaction equations for such materials [51–56]. Porous electrode theory and its application to intercalation cells (often referred to as *Newman's model*[57]) became a successful tool in industry [58] and science to investigate whole batteries or battery cells. Predicting the temperature generation, cell potential or degeneration allows for an estimation of cooling devices, autotimer electronics or lifetime on an engineering scale. At the end of 1990 $LiFePO_4$ as electrode material was identified[59], and its phase separating behavior laid the foundation of using phase-field methods in battery modeling. More and more sophisticated models, incorporating the non-ideal solution behavior as well as phase boundary contributions[60], were derived and became applicable due to growing computer power.
Similar enhancements of methods and models on the *interface level*[61–63] revealed the structure of the space charge region with unprecedented precision, slowly bridging the scale gap between the *cell level* and the *interface level*.
On the atomic level, developments in density functional theory[9] allow nowadays for the computation of chemical reaction pathways[64] as well as for material characterization[65], even in electrochemical systems.
Combining these methods, slowly an overall multi-scale theoretical approach to understand and investigate electrochemical systems is built up to face the big issues in battery development[66].[reprinted from 44]

3.1.2 Setup of a lithium ion battery

Before describing the actual modeling procedures, a brief overview of the setup of an intercalation battery is given.

Usually a battery (device) consists of a set of single batteries, control electronics, cooling devices and wiring which is called *system level*. Equivalent circuit models are used describe the system level as a control problem, *e.g.* to optimize the charging and discharging in hybrid electric cars.
A single battery is built out of a stack of cells, embedded in either a metallic shell (coin or round cells) or a pouch of special foil (pouch cell), which is called *stack level*. Classical questions, or optimization problems, arising on this scale are, *e.g.* the amount of the generated heat in operation, mechanical stability and aging effects. An overview of modeling procedures and the addressed issues on the *system* and *stack level* can be found in [67–76].
Conventional *cells* of a lithium ion intercalation battery consist of a porous anode and cathode, bathed in a liquid electrolyte and mixed with conductive filler and some binding material. The conductive filler ensures the electronic conductivity of the electrode mixture, since the active materials are commonly semiconductors, whereas the binding material glues the active particles and the conductivity enhancing particles together. Anode and cathode matrices are separated by a porous, electronic insulating membrane (separator)[77, 78], which is soaked by the liquid electrolyte to provide ionic conductivity.

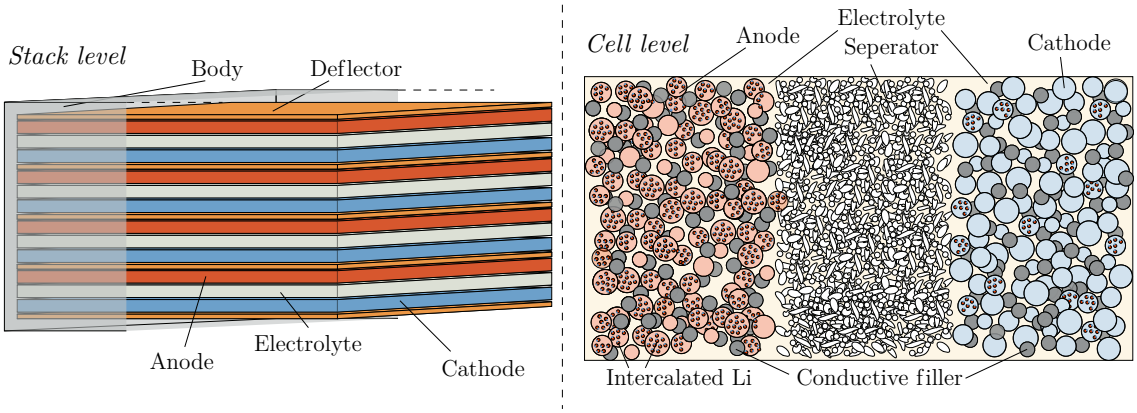

Figure 3.1.: (Left) *Stack level* of a lithium ion battery. The stack consists of several cells and is embedded into a rigid body. (Right) On the *cell level*, anode and cathode are porous materials mixed with a conductive filler and surrounded by the liquid electrolyte. The separator is a polymeric sponge soaked with liquid electrolyte. Reprinted from fig. 3 in [44].

The separator sponge also prevents convection of the liquid electrolyte and provides mechanical stability of the cell.[44]

A magnification of the actual interface between the surface of an electrode particle and the surrounding (liquid) electrolyte reveals the double layer structure or space charge region, generated by the mobile ions (see Fig. 3.2). The *interface level* covers this region in a porous electrode, and the later introduced *strong electroneutrality* condition allows for an implicit treatment of the *interface level* in the *cell level*. Electrochemical reactions on the actual surface of the electrode particle occur on the *atomic level* and are treated in this work with surface thermodynamics. The assumption of homogenous reactions throughout electrode particle surface allows then the incorporation of the *atomic level* in the *cell level* based volume averaging (or homogenization) methods.

Based on the derivation of the general thermo-electrodynamic equation framework of section 2 a consistent model of a porous intercalation cell is given in this chapter. In section 3.2 the electrolyte is modeled based on an incompressible mixture (*c.f.* section 2.9). The electrode is mathematically described in section 3.3 while in section 3.5 boundary conditions are derived to describe intercalation reactions. A conclusion is given in section 3.6 of the overall model equations.

3.2 Electrolyte

Electrolytes are commonly described in continuum mechanics with either Poisson–Nernst–Planck (PNP) equations, and its modifications[45, 46, 50, 61, 79–82], or generalizations of Ohm's law[51, 55]. Both of these descriptions can systematically be derived from non-equilibrium thermodynamics[44].

The electrolyte is explicitly modeled as an **incompressible** mixture ($n(\mathbf{y}, t) = \text{const.}$) with n = 3 species, *i.e.*

- anions A with mass density ρ_A and concentration c_A,
- cations C with mass density ρ_C and concentration c_C,

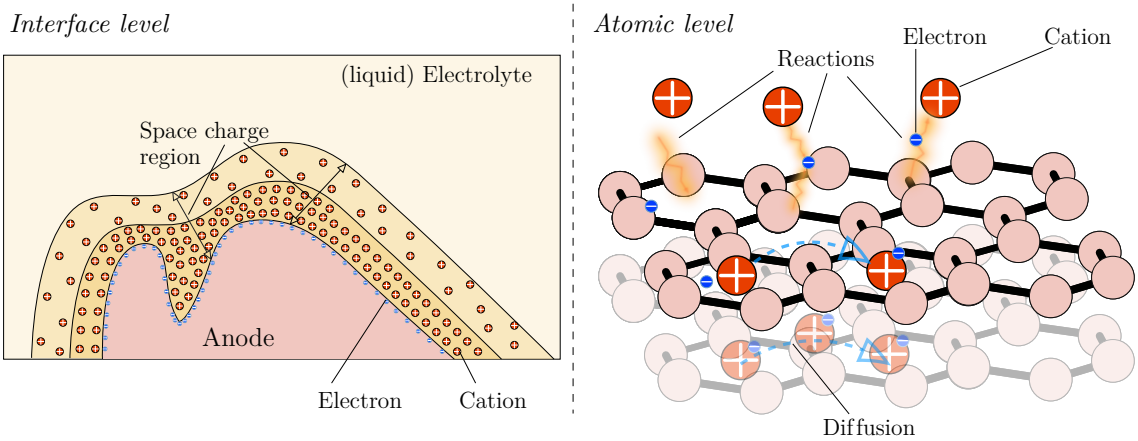

Figure 3.2.: (Left) At the interface between a charged anode particle and a liquid electrolyte a space charge region is formed due to the mobile cations in the electrolyte. (Right) On the *atomic level* the electrochemical reaction $\mathrm{C}^+ + \mathrm{e}^- \rightleftharpoons \mathrm{C}$ is treated as surface reaction. Reprint from fig. 4 in [44].

- and the solvent S with mass density ρ_S and concentration c_S. Throughout the further work c_S will be used as abbreviation for $1 - c_A - c_C = c_S$.[1]

In the variable setting $((T, p, c_A, c_C))$, the Gibbs free energy density (*c.f.* section 2.9) is

$$\mathfrak{g}(T, p, c_1, \ldots, c_{\mathrm{n}-1}) = \sum_{\alpha=1}^{\mathrm{n}} \overline{\mu}_\alpha^{\mathrm{R}} \cdot c_\alpha + n^{-1} \cdot p + k_{\mathrm{B}} T \sum_{\alpha=1}^{\mathrm{n}} c_\alpha \ln(c_\alpha) + T^2 \cdot C_T + \chi_{\mathrm{n}}^P \, \varepsilon_0^{-1} \mathbf{D} \cdot \mathbf{D}^{\mathrm{T}} \tag{3.1}$$

if polarization is taken into account. The chemical potential for each species is hence

$$\overline{\mu}_\alpha = \overline{\mu}_\alpha^{\mathrm{R}} + n^{-1} p + k_{\mathrm{B}} T \ln(c_\alpha) \qquad \alpha = 1, 2, 3. \tag{3.2}$$

Further, the electrolytic mixture is assumed to be non-reactive in the volume, *i.e.* chemical reactions only occur at the surface. However, if decomposition of an electrolyte salt or recombination of species is possible, this could be be modeled within a source term r_α [83]. The balance equations for the species densities are thus (*c.f.* 2.197)

$$\frac{\partial n_\alpha}{\partial t} = -\mathrm{div}\,(\rho_\alpha \mathbf{v} + \mathbf{j}_\alpha) \qquad \alpha = 1, \ldots, \mathrm{n} \tag{3.3}$$

$$n = \sum_{\alpha=1}^{3} n_\alpha. \tag{3.4}$$

For batteries, which operate at direct current, an electrostatic approximation of the electric flux density is quite appropriate. The electric field is then simply $\mathbf{E} = -\nabla\Phi$ where Φ the electrostatic potential. Constant polarization contributions $\mathbf{P} = \chi_{\mathrm{n}}^P \cdot \mathbf{D}$ lead to the Poisson equation

$$-\varepsilon_0 (1 + \chi^P) \mathrm{div}\, \nabla\Phi = n^{\mathrm{F}}. \tag{3.5}$$

Without any further assumptions, the full equation system would consist of

[1] Expressed as index set $\alpha = 1, \ldots, \mathrm{n}$ the anions correspond to $\alpha = 1$, cations to $\alpha = 2$ and the solvent to $\alpha = 3$.

- four balance equations to determine the anion and cation density as well as the pressure and temperature
- the momentum balance to determine the reference velocity field
- and the Poisson equation to determine the electrostatic potential.

To simplify the this coupled PDE system it is common to establish some material assumptions on the electrolyte:

- Incompressibility $\Rightarrow \overline{v} \equiv \text{const.}$
- No fluid convection $\Rightarrow \overline{\mathbf{v}} = \mathbf{0}$
- *Strong* electroneutrality: $n^{\mathrm{F}} = 0 \Rightarrow c_A = -\frac{z_C}{z_A} c_C$
- Constant coefficients in the resulting equation system.

3.2.1 Fluid assumptions

The setup of a common lithium ion battery cell is given in figure 3.1. Even though the electrolyte phase is liquid, in a real system the electrolyte domain is polymeric sponge, soaked with liquid electrolyte. From a mechanical point of view, the sponge provides mechanical stability. However, from a fluid dynamics point of view this implies that fluid is stationary. Regarding an appropriate choice of coordinate system one thus uses $((\mathbf{y}, \overline{\mathbf{v}}))$ as reference coordinate system, which obeys[2]

$$\frac{\partial n}{\partial t} = -\mathrm{div}\,(n\overline{\mathbf{v}}) \tag{3.6}$$

$$\sum_{\alpha=1}^{\mathrm{n}} \bar{\mathbf{j}}_\alpha = \mathbf{0}. \tag{3.7}$$

Due to the sponge, the convective part vanishes, *i.e.* $\overline{\mathbf{v}} = \mathbf{0}$, and the material model (3.1) implies

$$\kappa_p = 0, \tag{3.8}$$

i.e. incompressibility. Equation (3.6) is thus trivially satisfied, and due to $\overline{\mathbf{v}} = \mathbf{0}$ the remaining balance equations for the species α

$$\frac{\partial n_\alpha}{\partial t} = -\mathrm{div}\,\bar{\mathbf{j}}_\alpha \qquad \alpha = 1, 2, 3 \tag{3.9}$$

decouple from the momentum balance (2.207). Since the specific enthalpy

$$\mathfrak{h}_\alpha = \overline{\mu}_\alpha - T\frac{\partial \overline{\mu}_\alpha}{\partial T} = \overline{\mu}_\alpha^{\mathrm{R}} = \text{const.} \tag{3.10}$$

for the assumed mixture, the heat equation (2.438) is simply

$$-C_T \cdot \frac{\partial T}{\partial t} = -\mathrm{div}\,\bar{\mathbf{j}}_\vartheta + \frac{1}{T}\mathbf{j}^{\mathrm{F}} \cdot \nabla\Phi \tag{3.11}$$

[2]Note that in general $n = n(T, p)$, *c.f.* section 2.8.3 on the pressure equation.

with the heat flux (*c.f.* eq. 2.440)

$$\bar{\mathbf{j}}_\vartheta = \frac{1}{T}\left(\bar{\mathbf{j}}_u - \sum_{\alpha=1}^{\mathrm{n}} \overline{\mu}_\alpha \bar{\mathbf{j}}_\alpha\right) \tag{3.12}$$

and a constant heat capacity C_T. The only heat source in the electrolyte region is thus due to an electric current (electric heating), even though governed by ions, not by electrons.

A thermodynamic consistent choice of the fluxes $\bar{\mathbf{j}}_u$, $\bar{\mathbf{j}}_A$ and $\bar{\mathbf{j}}_C$, according to theorem 9, is

$$\begin{pmatrix} -\bar{\mathbf{j}}_u \\ \bar{\mathbf{j}}_A \\ \bar{\mathbf{j}}_C \end{pmatrix} = -\begin{pmatrix} \mathbf{L}_{\vartheta,\vartheta} & \mathbf{L}_{\vartheta,A} & \mathbf{L}_{\vartheta,C} \\ \mathbf{L}_{\vartheta,A} & \mathbf{L}_{A,A} & \mathbf{L}_{A,C} \\ \mathbf{L}_{\vartheta,C} & \mathbf{L}_{C,A} & \mathbf{L}_{C,C} \end{pmatrix} \cdot \begin{pmatrix} \nabla \frac{1}{T} \\ \nabla \frac{\mu_A - \mu_S}{T} - \frac{e_0\, z_A}{T} \nabla\Phi \\ \nabla \frac{\mu_C - \mu_S}{T} - \frac{e_0\, z_C}{T} \nabla\Phi \end{pmatrix} \tag{3.13}$$

$$= -\begin{pmatrix} \mathbf{L}_{\vartheta,\vartheta} & \mathbf{L}_{\vartheta,A} & \mathbf{L}_{\vartheta,C} \\ \mathbf{L}_{\vartheta,A} & \mathbf{L}_{A,A} & \mathbf{L}_{A,C} \\ \mathbf{L}_{\vartheta,C} & \mathbf{L}_{C,A} & \mathbf{L}_{C,C} \end{pmatrix} \cdot \begin{pmatrix} \nabla \frac{1}{T} \\ k_\mathrm{B}\, \nabla \ln\left(\frac{c_A}{c_S}\right) - \frac{e_0\, z_A}{T} \nabla\Phi \\ k_\mathrm{B}\, \nabla \ln\left(\frac{c_C}{c_S}\right) - \frac{e_0\, z_C}{T} \nabla\Phi \end{pmatrix} \tag{3.14}$$

with a symmetric, positive definite matrix $\underline{\underline{\mathbf{L}}}$. Recall that each component $\mathbf{L}_{\alpha,\beta}$ of $\underline{\underline{\mathbf{L}}}$ is itself a matrix (Onsager coefficient) and assumed to be invertible. The flux of the solvent species is simply obtained from the flux constraint (3.7) as

$$\bar{\mathbf{j}}_S = -\bar{\mathbf{j}}_A - \bar{\mathbf{j}}_C. \tag{3.15}$$

The representation 3.13 of the fluxes is the most general version of the Nernst–Planck flux with $\mathbf{L}_{A,A}$, $\mathbf{L}_{A,C}$, and $\mathbf{L}_{C,C}$ as independent Onsager coefficients for the material flux. For vanishing cross-coefficients $\mathbf{L}_{A,C} = 0$ the Nernst–Planck-flux for the species A further simplifies to

$$\bar{\mathbf{j}}_A = -\mathbf{L}_{A,\theta} \nabla \frac{1}{T} - k_\mathrm{B}\, \mathbf{L}_{A,A} \cdot \left(\left(\frac{c_S}{c_A} - \frac{1}{c_S}\right) \nabla c_A - \frac{1}{c_S} \nabla c_C - \frac{e_0 z_A}{k_\mathrm{B} T} \nabla\Phi\right), \tag{3.16}$$

where the Onsager coefficient $\mathbf{L}_{A,A}$ is called mobility, and similar relation of course holds for the species C.

For the so called dilute limit[53], in which the species densities of n_A and n_C with respect to the overall density n are tiny, the solvent concentration $c_S \approx 1$ and the $\ln\left(\frac{c_\alpha}{c_S}\right) \approx \ln(c_\alpha)$. The **dilute limit Nernst–Planck flux** is hence

$$\bar{\mathbf{j}}_\alpha^{\mathrm{dilute}} = -\mathbf{L}_{\alpha,\theta} \nabla \frac{1}{T} - k_\mathrm{B}\, \mathbf{L}_{\alpha,\alpha} \cdot \left(\frac{1}{c_\alpha} \nabla c_\alpha - \frac{e_0 z_\alpha}{k_\mathrm{B} T} \nabla\Phi\right) \tag{3.17}$$

$$= -\mathbf{L}_{\alpha,\theta} \nabla \frac{1}{T} - \mathbf{D}^{\mathrm{dilute}} \cdot \left(\nabla c_A - \frac{e_0 z_\alpha}{k_\mathrm{B} T}\, c_\alpha \cdot \nabla\Phi\right) \tag{3.18}$$

where $\mathbf{D}^{\mathrm{dilute}}$ is the dilute diffusion coefficient obtained from the Einstein–Smoluchowski relationship [84, 85]. It is the common basis for modeling approaches with Poisson–Nernst–Planck [50, 79, 80, 86–89] and Poisson–Boltzmann (PB) equations [45, 81, 90, 91] . Note, however, that this simplification violates the incompressibility of the liquid electrolyte [36], and is actually only valid for plasma.

3.2.2 Strong electroneutrality assumption

The most common approach to simplify the whole equation system is the so called electroneutrality condition[92]. It is assumed that charge separation between cations and anions does not occur, even in the density formulation. I introduced the terminology *strong electroneutrality* [44], *i.e.*

$$n^{\mathrm{F}} = n \cdot (z_A c_A + z_C c_C) = 0 \quad \forall\, (\mathbf{y}, t) \in \Omega \times I, \tag{3.19}$$

in order to distinguish the assumption from general valid global (or weak) electroneutrality

$$\int_{\Omega} n^{\mathrm{F}}(\mathbf{x})\, d\mathbf{x} = 0. \tag{3.20}$$

This concept neglects the space charge region at the electrode/electrolyte interface[51, 55]. However, this problem or inaccuracy can be corrected, with some limitations, by treating the space charge region and its influence implicitly with the introduction of an *electrochemical potential of charge* (cf. eq. 3.32.). The assumption is crucial and still in discussion [92–96] as it smears out any structural roughness, spikes or curvatures of the electrode/electrolyte interface on the nm scale[88]. However, almost all approaches in battery modeling relay on the strong electroneutrality assumption [3, 55, 56, 97–111].

To apply the assumption $n^{\mathrm{F}} = 0$ one performs first the variable transformation $c_C \to n^{\mathrm{F}}$ and hence choose $(T, p, c_A, n^{\mathrm{F}})$ as independent properties. Reconsidering the initial entropy function[3] with the suggested variable change

$$n \cdot s = \bar{\mathfrak{s}}(n \cdot u, n_A, n_C, n_S) \tag{3.22}$$

$$= \mathfrak{s}(n \cdot u, n_A, \frac{1}{e_0\, z_C} \cdot \left(n^{\mathrm{F}} - e_0 z_A \cdot n_A\right), n_S) \tag{3.23}$$

leads to the entropy balance

$$\frac{\partial\, n \cdot s}{\partial\, t} = -\frac{1}{T} \cdot \frac{\partial\, n \cdot u}{\partial\, t} - \frac{\overline{\mu}_C}{T} \cdot \frac{1}{e_0\, z_C} \cdot \left(\frac{\partial\, n^{\mathrm{F}}}{\partial\, t} - e_0 z_A \cdot \frac{\partial\, n_A}{\partial\, t}\right) - \frac{\overline{\mu}_A}{T}\frac{\partial\, n_A}{\partial\, t} - \frac{\overline{\mu}_S}{T}\frac{\partial\, n_S}{\partial\, t} \tag{3.24}$$

$$= -\frac{1}{T} \cdot \frac{\partial\, n \cdot u}{\partial\, t} - \frac{\overline{\mu}_C}{e_0 z_C\, T} \cdot \frac{\partial\, n^{\mathrm{F}}}{\partial\, t} - \frac{(\overline{\mu}_A - \frac{z_A}{z_C}\overline{\mu}_C)}{T}\frac{\partial\, n_C}{\partial\, t} - \frac{\overline{\mu}_S}{T}\frac{\partial\, n_S}{\partial\, t}. \tag{3.25}$$

In the frame of reference $(\mathbf{y}, \overline{\mathbf{v}})$ one obtains, with the charge conservation equation

$$\frac{\partial\, n^{\mathrm{F}}}{\partial\, t} = -\mathrm{div}\, \bar{\mathbf{j}}^{\mathrm{F}} \tag{3.26}$$

and the flux constraint

$$\bar{\mathbf{j}} = -\bar{\mathbf{j}}_A - \bar{\mathbf{j}}_C, \tag{3.27}$$

[3]Note that throughout this section the entropy function is considered per particles, *i.e.*

$$S = \int_{\Omega} n\, s\, d\mathbf{x}. \tag{3.21}$$

the entropy balance

$$\frac{\partial\, n\cdot s}{\partial\, t} = -\mathrm{div}\,\bar{\mathbf{j}}_s + \mathbf{j}_u^{\mathrm{T}}\cdot\nabla\frac{1}{T} + \bar{\mathbf{j}}^{\mathrm{F}\,\mathrm{T}}\cdot\left(\frac{1}{T}\nabla\Phi - \nabla\frac{\overline{\mu}_C-\overline{\mu}_S}{e_0 z_C\, T}\right)$$
$$-\bar{\mathbf{j}}_A^{\mathrm{T}}\cdot\left(\nabla\frac{\overline{\mu}_A-\overline{\mu}_S}{T} - \frac{z_A}{e_0 z_C}\nabla\frac{\overline{\mu}_C-\overline{\mu}_S}{T}\right). \tag{3.28}$$

Some rearrangement according to AC 3.41 and the introduction of the alternative internal energy flux

$$\widetilde{\mathbf{j}}_u := \bar{\mathbf{j}}_u - \bar{\mathbf{j}}^{\mathrm{F}}\cdot\frac{\overline{\mu}_C-\overline{\mu}_S}{e_0 z_C} \tag{3.29}$$

leads to the entropy production

$$\overline{r}_s = \widetilde{\mathbf{j}}_u^{\mathrm{T}}\cdot\nabla\frac{1}{T} + \frac{1}{T}\cdot\bar{\mathbf{j}}^{\mathrm{F}\,\mathrm{T}}\cdot\nabla\left(\Phi - \frac{\overline{\mu}_C-\overline{\mu}_S}{e_0 z_C}\right) - \bar{\mathbf{j}}_A^{\mathrm{T}}\cdot\left(\nabla\frac{\overline{\mu}_A-\overline{\mu}_S}{T} - \frac{z_A}{e_0 z_C}\nabla\frac{\overline{\mu}_C-\overline{\mu}_S}{T}\right). \tag{3.30}$$

Auxiliary calculation 3.41:

$$\bar{\mathbf{j}}_u^{\mathrm{T}}\cdot\nabla\frac{1}{T} - \bar{\mathbf{j}}^{\mathrm{F}\,\mathrm{T}}\cdot\nabla\frac{\overline{\mu}_C-\overline{\mu}_S}{e_0 z_C\, T} = \left(\underbrace{\bar{\mathbf{j}}_u^{\mathrm{T}} - \bar{\mathbf{j}}^{\mathrm{F}}\cdot\frac{\overline{\mu}_C-\overline{\mu}_S}{e_0 z_C}}_{=:\widetilde{\mathbf{j}}_u}\right)\cdot\nabla\frac{1}{T} - \frac{1}{T}\bar{\mathbf{j}}^{\mathrm{F}\,\mathrm{T}}\cdot\nabla\frac{\overline{\mu}_C-\overline{\mu}_S}{e_0 z_C}$$

According to theorem 9 one could thus choose the fluxes as

$$\begin{pmatrix} -\widetilde{\mathbf{j}}_u \\ -\bar{\mathbf{j}}^{\mathrm{F}} \\ \bar{\mathbf{j}}_A \end{pmatrix} = -\begin{pmatrix} \widetilde{\mathbf{L}}_{\vartheta,\vartheta} & \widetilde{\mathbf{L}}_{\vartheta,F} & \widetilde{\mathbf{L}}_{\vartheta,A} \\ \widetilde{\mathbf{L}}_{\vartheta,F} & \widetilde{\mathbf{L}}_{F,F} & \widetilde{\mathbf{L}}_{F,A} \\ \widetilde{\mathbf{L}}_{\vartheta,A} & \widetilde{\mathbf{L}}_{A,F} & \widetilde{\mathbf{L}}_{A,A} \end{pmatrix}\cdot\begin{pmatrix} \nabla\frac{1}{T} \\ \nabla\left(\Phi - \frac{\overline{\mu}_C-\overline{\mu}_S}{e_0 z_C}\right) \\ \nabla\frac{\overline{\mu}_A-\overline{\mu}_S}{T} - \nabla\frac{z_A}{z_C}\cdot\left(\frac{\overline{\mu}_C-\overline{\mu}_S}{T}\right) \end{pmatrix} \tag{3.31}$$

with a symmetric, positive definite Onsager matrix $(\widetilde{\mathbf{L}}_{\alpha,\beta})_{\alpha,\beta=\vartheta,F,C}$ to ensure the local second law. This structure is quite remarkable, which is shown more clearly with the following abbreviations. The conjugate variable of an electric current is obviously

$$\Phi + \frac{\overline{\mu}_C-\overline{\mu}_S}{e_0 z_C} =: \widetilde{\Phi}, \tag{3.32}$$

which covers *all* electrostatic effects in the electrolyte. One could thus *carefully* call $\widetilde{\Phi}$ **electrochemical potential of charge** (or potential of an electric current). In accordance, the thermodynamic driving force for the anion flux is

$$\frac{\overline{\mu}_A-\overline{\mu}_S}{T} - \frac{z_A}{z_C}\cdot\left(\frac{\overline{\mu}_C-\overline{\mu}_S}{T}\right) =: \widetilde{\mu}, \tag{3.33}$$

and $\widetilde{\mu}$ is called **effective chemical potential** of the anions. Similar $\widetilde{\mu}$ implicitly covers also effects arising from the cations.

Reconsidering the heat equation, one obtains in the new variables gives

$$-C_T \cdot \frac{\partial T}{\partial t} = -\operatorname{div}\left(\frac{1}{T}\widetilde{\mathbf{j}}_u\right) + \frac{1}{T}\bar{\mathbf{j}}^{\mathrm{F}\,\mathrm{T}} \cdot \nabla\widetilde{\Phi} - \frac{\overline{\mu}_C - \overline{\mu}_S}{e_0 z_C} \cdot \bar{\mathbf{j}}^{\mathrm{F}\,\mathrm{T}} \cdot \nabla\frac{1}{T} - \left(\frac{\overline{\mu}_C - \overline{\mu}_S}{e_0 z_C\, T}\right) \cdot \operatorname{div}\bar{\mathbf{j}}^{\mathrm{F}} \tag{3.34}$$

$$= -\operatorname{div}\frac{1}{T}\left(\widetilde{\mathbf{L}}_{\vartheta,\vartheta} \cdot \nabla\frac{1}{T} + \widetilde{\mathbf{L}}_{\vartheta,F} \cdot \nabla\widetilde{\Phi} + \widetilde{\mathbf{L}}_{\vartheta,A} \cdot \nabla\widetilde{\mu}\right) + r_\vartheta. \tag{3.35}$$

Auxiliary calculation 3.42:

$$\begin{aligned}
-\operatorname{div}\left(\frac{1}{T}\mathbf{j}_u\right) + \frac{1}{T}\bar{\mathbf{j}}^{\mathrm{F}} \cdot \nabla\Phi &= -\operatorname{div}\left(\frac{1}{T}\left(\widetilde{\mathbf{j}}_u + \bar{\mathbf{j}}^{\mathrm{F}} \cdot \frac{\overline{\mu}_C - \overline{\mu}_S}{e_0 z_C}\right)\right) + \bar{\mathbf{j}}^{\mathrm{F}\,\mathrm{T}} \cdot \nabla\Phi \\
&= -\operatorname{div}\frac{1}{T}\widetilde{\mathbf{j}}_u + \frac{1}{T}\bar{\mathbf{j}}^{\mathrm{F}\,\mathrm{T}} \cdot \nabla\left(\Phi - \frac{\overline{\mu}_C - \overline{\mu}_S}{e_0 z_C}\right) - \frac{\overline{\mu}_C - \overline{\mu}_S}{e_0 z_C}\operatorname{div}\frac{1}{T}\bar{\mathbf{j}}^{\mathrm{F}} \\
&= -\operatorname{div}\frac{1}{T}\widetilde{\mathbf{j}}_u + \frac{1}{T}\bar{\mathbf{j}}^{\mathrm{F}\,\mathrm{T}} \cdot \nabla\widetilde{\Phi} - \frac{\overline{\mu}_C - \overline{\mu}_S}{e_0 z_C}\bar{\mathbf{j}}^{\mathrm{F}} \cdot \nabla\frac{1}{T} - \left(\frac{\overline{\mu}_C - \overline{\mu}_S}{e_0 z_C\, T}\right)\operatorname{div}\bar{\mathbf{j}}^{\mathrm{F}}
\end{aligned}$$

Inserting the actual flux representations leads to the balance equation for n^{F} and n_A (or c_A) as

$$\frac{\partial n^{\mathrm{F}}}{\partial t} = -\operatorname{div}\left(\widetilde{\mathbf{L}}_{\vartheta,F} \cdot \nabla\frac{1}{T} + \widetilde{\mathbf{L}}_{F,F} \cdot \nabla\widetilde{\Phi} + \widetilde{\mathbf{L}}_{F,A} \cdot \nabla\widetilde{\mu}\right) \tag{3.36}$$

$$\frac{\partial n_A}{\partial t} = \operatorname{div}\left(\widetilde{\mathbf{L}}_{\vartheta,A} \cdot \nabla\frac{1}{T} + \widetilde{\mathbf{L}}_{A,F} \cdot \nabla\widetilde{\Phi} + \widetilde{\mathbf{L}}_{A,A} \cdot \nabla\widetilde{\mu}\right). \tag{3.37}$$

Note that in the whole coupled equation system the electrostatic potential Φ is not explicitly present anymore. If the corresponding boundary conditions can also be formulated without an explicit occurrence of Φ, but in terms of $\widetilde{\Phi}$, one has **decoupled the flux equations from the Poisson equation**, in the sense that the Poisson equation is not required anymore to compute an unknown variable of the equation system.

Next, strong electroneutrality $n^{\mathrm{F}} = 0$ is assumed, which implies

$$c_A = -\underbrace{\frac{z_C}{z_A}}_{\bar{z}} c_C \tag{3.38}$$

and

$$-\operatorname{div}\bar{\mathbf{j}}^{\mathrm{F}} = 0. \tag{3.39}$$

This could be further exploited to simplify the remaining equation system. Rearranging the relation for the electric current

$$\bar{\mathbf{j}}^{\mathrm{F}} = \widetilde{\mathbf{L}}_{\vartheta,F} \cdot \nabla\frac{1}{T} + \widetilde{\mathbf{L}}_{F,F} \cdot \nabla\widetilde{\Phi} + \widetilde{\mathbf{L}}_{F,A} \cdot \nabla\widetilde{\mu} \tag{3.40}$$

as

$$\nabla\widetilde{\Phi} = \widetilde{\mathbf{L}}_{F,F}^{-1} \cdot \bar{\mathbf{j}}^{\mathrm{F}} - \widetilde{\mathbf{L}}_{F,F}^{-1} \cdot \widetilde{\mathbf{L}}_{\vartheta,F} \cdot \nabla\frac{1}{T} - \widetilde{\mathbf{L}}_{F,F}^{-1} \cdot \widetilde{\mathbf{L}}_{F,A} \cdot \nabla\widetilde{\mu} \tag{3.41}$$

leads to the representation of the balance equation system

$$
\begin{aligned}
-C_T \cdot \frac{\partial T}{\partial t} &= \operatorname{div} \frac{1}{T} \left((\widetilde{\mathbf{L}}_{\vartheta,\vartheta} - \widetilde{\mathbf{L}}_{F,F}^{-1} \cdot \widetilde{\mathbf{L}}_{\vartheta,F}^{2}) \cdot \nabla \frac{1}{T} + (\widetilde{\mathbf{L}}_{\vartheta,A} - \widetilde{\mathbf{L}}_{\vartheta,F} \cdot \widetilde{\mathbf{L}}_{F,F}^{-1} \cdot \widetilde{\mathbf{L}}_{F,A}) \cdot \nabla \widetilde{\mu} \right) \\
&\quad + \operatorname{div} (\widetilde{\mathbf{L}}_{F,F}^{-1} \cdot \widetilde{\mathbf{L}}_{\vartheta,F} \cdot \overline{\mathbf{j}}^{\mathrm{F}}) + r_\vartheta && (3.42) \\
0 &= -\operatorname{div} \overline{\mathbf{j}}^{\mathrm{F}} && (3.43) \\
\frac{\partial n_A}{\partial t} &= \operatorname{div} \left((\widetilde{\mathbf{L}}_{\vartheta,A} - \widetilde{\mathbf{L}}_{F,F}^{-1} \cdot \widetilde{\mathbf{L}}_{\vartheta,F} \cdot \widetilde{\mathbf{L}}_{A,F}) \cdot \nabla \frac{1}{T} + (\widetilde{\mathbf{L}}_{A,A} - \widetilde{\mathbf{L}}_{F,F}^{-1} \cdot \widetilde{\mathbf{L}}_{F,A}^{2}) \cdot \nabla \widetilde{\mu} \right) \\
&\quad + \operatorname{div} \left(\widetilde{\mathbf{L}}_{A,F} \cdot \widetilde{\mathbf{L}}_{F,F}^{-1} \cdot \overline{\mathbf{j}}^{\mathrm{F}} \right). && (3.44)
\end{aligned}
$$

For the further derivation it is necessary to explicitly compute $\nabla \widetilde{\mu}$.

Auxiliary calculation 3.43:

$$
\begin{aligned}
\widetilde{\mu} &= \frac{\overline{\mu}_A - \overline{\mu}_S}{T} - \frac{z_A}{z_C} \cdot (\frac{\overline{\mu}_C - \overline{\mu}_S}{T}) = k_{\mathrm{B}} \left(\ln(c_A) - (1 - \frac{z_A}{z_C}) \ln(c_S) - \frac{z_A}{z_C} \ln(c_C) \right) \\
&= k_{\mathrm{B}} \left(\ln(c_A) - (1 - \overline{z}) \ln(1 - (1 - \overline{z}) c_A) + \overline{z} \ln(-\overline{z} c_A) \right)^{4}
\end{aligned}
$$

Building hence the gradient of $\widetilde{\mu}$ leads to

$$
\begin{aligned}
\nabla \widetilde{\mu} &= k_{\mathrm{B}} \left(\frac{1}{c_A} \nabla c_A + \frac{(1 - \overline{z})^2}{1 - (1 - \overline{z}) c_A} \nabla c_A + \overline{z} \nabla c_A \right) \\
&= \frac{\partial \widetilde{\mu}(c_A)}{\partial c_A} \nabla c_A
\end{aligned}
$$

It is quite convenient now to introduce abbreviations for the products of Onsager coefficients. Isotropy is now **assumed** throughout the electrolyte with which the Onsager coefficients become scalars. Common abbreviations are [111]

- the heat conductivity $\kappa_T = \widetilde{\mathbf{L}}_{\vartheta,\vartheta}$,
- the Seebeck coefficient $\kappa_\vartheta = \widetilde{\mathbf{L}}_{\vartheta,F}$,
- the Soret coefficient $\gamma_\vartheta = \widetilde{\mathbf{L}}_{\vartheta,A}$,
- the transference number $t_A = e_0 \cdot \widetilde{\mathbf{L}}_{A,F} \cdot \widetilde{\mathbf{L}}_{F,F}^{-1}$ with $t_A = 1 - t_C$,[5]
- the chemical diffusion coefficient of species A

$$
D_A = \frac{\partial \widetilde{\mu}}{\partial c_A} \cdot \left(\widetilde{\mathbf{L}}_{A,A} - \widetilde{\mathbf{L}}_{F,F}^{-1} \cdot \widetilde{\mathbf{L}}_{F,A}^{2} \right), \tag{3.45}
$$

- and the (electrical) conductivity $\kappa_F = \widetilde{\mathbf{L}}_{F,F}$.

Common assumption[53] on the material coefficients are now

$$
\begin{aligned}
\kappa_T &= \text{const.} && (3.46) \\
\kappa_\vartheta &= \text{const.} && (3.47) \\
t_A &= \text{const.} && (3.48)
\end{aligned}
$$

[4] Note that $\overline{z} < 0$ and $c_A > 0$ with which $\ln(-\overline{z})$ is well defined.
[5] Note that this follows directly from the strong electroneutrality condition.

which essentially decouples the balance equation system. The main trick is surely to exploit $\operatorname{div}\bar{\mathbf{j}}^{\mathrm{F}} = 0$ (due to the constant parameters) in equation (3.42) and (3.44) which results in the balance equations

$$-C_T\,T\cdot\frac{\partial T}{\partial t} = -\operatorname{div}\left((\kappa_T+\kappa_F^{-1}\cdot\kappa_\vartheta^2)\nabla\frac{1}{T}+(\gamma_\vartheta-t_A\cdot\kappa_\vartheta)\cdot\frac{\partial\,\widetilde{\mu}(c_A)}{\partial\,c_A}\cdot\nabla c_A\right)+r_\vartheta \tag{3.49}$$

$$0 = -\operatorname{div}\left(\kappa_\vartheta\nabla\frac{1}{T}+\kappa_F\nabla\widetilde{\Phi}+t_A\cdot\kappa_F\frac{\partial\,\widetilde{\mu}(c_A)}{\partial\,c_A}\nabla c_A\right) \tag{3.50}$$

$$\frac{\partial\,n_A}{\partial\,t} = \operatorname{div}\left((\gamma_\vartheta-t_A\cdot\kappa_\vartheta)\cdot\nabla\frac{1}{T}+D_A\nabla c_A\right), \tag{3.51}$$

with the heat source (*c.f.* AC 3.44)

$$\begin{aligned} r_\vartheta = {} & \frac{k_{\mathrm{B}}T}{e_0 z_C}\ln\left(\frac{c_S}{c_A}\right)\cdot\left(\kappa_\vartheta\nabla(\frac{1}{T})^2+t_A\cdot\kappa_F\frac{\partial\,\widetilde{\mu}(c_A)}{\partial\,c_A}\left\langle\nabla c_A,\nabla\frac{1}{T}\right\rangle\right) \\ & +\frac{1}{T}\cdot\left(\kappa_F(\nabla\widetilde{\Phi})^2+t_A\cdot\kappa_F\frac{\partial\,\widetilde{\mu}(c_A)}{\partial\,c_A}\left\langle\nabla\widetilde{\Phi},\nabla c_A\right\rangle\right)+\left(\frac{\kappa_\vartheta}{T}+\frac{k_{\mathrm{B}}T}{e_0 z_C}\kappa_F\right)\cdot\left\langle\nabla\widetilde{\Phi},\nabla\frac{1}{T}\right\rangle. \end{aligned} \tag{3.52}$$

Auxiliary calculation 3.44: Heat source

$$\bar{\mathbf{j}}^{\mathrm{F}_{\mathrm{T}}}\cdot\nabla\widetilde{\Phi} = \kappa_\vartheta\left\langle\nabla\widetilde{\Phi},\nabla\frac{1}{T}\right\rangle+\kappa_F(\nabla\widetilde{\Phi})^2+t_A\cdot\kappa_F\frac{\partial\,\widetilde{\mu}(c_A)}{\partial\,c_A}\left\langle\nabla\widetilde{\Phi},\nabla c_A\right\rangle$$

$$\bar{\mathbf{j}}^{\mathrm{F}_{\mathrm{T}}}\cdot\nabla\frac{1}{T} = \kappa_\vartheta\nabla(\frac{1}{T})^2+\kappa_F\left\langle\nabla\widetilde{\Phi},\nabla\frac{1}{T}\right\rangle+t_A\cdot\kappa_F\frac{\partial\,\widetilde{\mu}(c_A)}{\partial\,c_A}\left\langle\nabla c_A,\nabla\frac{1}{T}\right\rangle$$

With

$$-\frac{\overline{\mu}_C-\overline{\mu}_S}{e_0 z_C} = \frac{k_{\mathrm{B}}T}{e_0 z_C}\ln\left(\frac{c_S}{c_A}\right)$$

The overall heat source is thus

$$\begin{aligned} r_\vartheta &= \frac{1}{T}\bar{\mathbf{j}}^{\mathrm{F}_{\mathrm{T}}}\cdot\nabla\widetilde{\Phi}-\frac{\overline{\mu}_C-\overline{\mu}_S}{e_0 z_C}\cdot\bar{\mathbf{j}}^{\mathrm{F}_{\mathrm{T}}}\cdot\nabla\frac{1}{T} \\ &= \frac{1}{T}\cdot\left(\kappa_\vartheta\left\langle\nabla\widetilde{\Phi},\nabla\frac{1}{T}\right\rangle+\kappa_F(\nabla\widetilde{\Phi})^2+t_A\cdot\kappa_F\frac{\partial\,\widetilde{\mu}(c_A)}{\partial\,c_A}\left\langle\nabla\widetilde{\Phi},\nabla c_A\right\rangle\right) \\ &\quad+\frac{k_{\mathrm{B}}T}{e_0 z_C}\ln\left(\frac{c_S}{c_A}\right)\cdot\left(\kappa_\vartheta\left(\nabla\frac{1}{T}\right)^2+\kappa_F\left\langle\nabla\widetilde{\Phi},\nabla\frac{1}{T}\right\rangle+t_A\cdot\kappa_F\frac{\partial\widetilde{\mu}(c_A)}{\partial\,c_A}\left\langle\nabla c_A,\nabla\frac{1}{T}\right\rangle\right) \\ &= \frac{k_{\mathrm{B}}T}{e_0 z_C}\ln\left(\frac{c_S}{c_A}\right)\cdot\left(\kappa_\vartheta\nabla(\frac{1}{T})^2+t_A\cdot\kappa_F\frac{\partial\,\widetilde{\mu}(c_A)}{\partial\,c_A}\left\langle\nabla c_A,\nabla\frac{1}{T}\right\rangle\right) \\ &\quad+\frac{1}{T}\cdot\left(\kappa_F(\nabla\widetilde{\Phi})^2+t_A\cdot\kappa_F\frac{\partial\,\widetilde{\mu}(c_A)}{\partial\,c_A}\left\langle\nabla\widetilde{\Phi},\nabla c_C\right\rangle\right) \\ &\quad+\left(\frac{\kappa_\vartheta}{T}+\frac{k_{\mathrm{B}}T}{e_0 z_C}\kappa_F\right)\cdot\left\langle\nabla\widetilde{\Phi},\nabla\frac{1}{T}\right\rangle \end{aligned}$$

It is noteworthy that equation (3.51) is essentially a **diffusion equation** for species A (or similar for the species C due to the strong electroneutrality condition) and thus a linear PDE, in contrast to the fully non-linear Poisson–Nernst–Planck representation (3.16). Equation (3.50) is called **generalized Ohmic law**, which determines the electrochemical potential of charge $\widetilde{\Phi}$. It does **not** determine the electrostatic potential Φ. There is a quite longstanding discussion in literature *what* $\widetilde{\Phi}$ actually is[53, 93–95]. Due

to the electroneutrality condition one could simply think of $\widetilde{\Phi}$ as being the electrostatic potential *outside the space charge region.* Other authors[3] interpret $\widetilde{\Phi}$ as the *measured potential with a (lithium) reference electrode in solution.* Anyhow, the electroneutrality is, like the incompressibility, a remarkable assumption with drastic implications and simplifications. From a computational point of view the above strategy linearizes and decouples a (in general) highly non-linear PDE system. In addition, one balance equation becomes stationary, which allows for a recursive insertion of the solution in transient numerical schemes.

As already mentioned, the strategy *works* if the reaction boundary conditions can exclusively be described in the potentials $\widetilde{\Phi}$ and $\widetilde{\mu}$. In section 3.5 a derivation of reaction boundary conditions based on surface reactions is given which indeed leads to a reaction rate based on $\widetilde{\Phi}$ and $\widetilde{\mu}$, in addition to the potential in the electrode phase.

3.3 Electrode

Continuum mechanical modeling of intercalation electrodes separates into two branches, electrode particle models and the porous electrode theory. While in the first branch each electrode particle is considered and spatially resolved, the latter one treats the (porous) electrode with volume averaging strategies and thus neglects the specific microstructure. Historically the porous electrode model was developed to enable computational access to the cell level with moderate computer power. By neglecting the actual microscopic structure of a porous electrode, the model simplifies from 3-D to 1-D, reducing the computational time from $\mathcal{O}(\mathcal{N}^9)$ to $\mathcal{O}(\mathcal{N}^3)$, where $\mathcal{N}$ is the number of elements in one dimension. Recent developments in material science, *e.g.* 3-D computer tomographic investigations[112] or combined FIB/SEM methods[113–115] reveal the actual microstructure on the μm to 100 nm scale and allow for a reconstruction as finite element mesh[116]. This allows for full 3-D simulations of the electrodes and the surrounding electrolyte to investigate local ion flux and current densities, heat generation hotspots *etc.*[117]. Of course, the computational cost for 3-D diffusion-migration simulations on highly porous geometries is not negligible. Modern numerical methods such as adaptive finite element or finite volume methods serve as a basis for a reasonable computational expenditure[81, 118]. Further, full 3-D simulations can serve as a benchmark for simplified volume averaged electrode models to either quantify the simplification error or refine an averaged model appropriately.[44]

3.3.1 Electrode particle models

Diffusion of lithium in single electrode particles is classically modeled with simple diffusion equations to describe the status of charge (SOC) of an electrode particle or the whole electrode[53]. Recent experimental investigations of a wide class of electrode materials revealed phase separation phenomena during charging and discharging[119], which cannot be predicted by a simple diffusion equations. This also implies that *open circuit potential*, which is introduced below, can **not** self-consistently be incorporated by such a class of model. More general approaches based on phase field models[60, 120] are yet at the very beginning to actually predict the open circuit potential, which is of course a central property of a lithium ion battery cell[2].

An electrode material is modeled here with a free energy function containing a lattice configurational entropy. The lattice is assumed to remain fixed (*i.e.* n_ℓ = const. and n_ℓ thus arises only as parameter), and the remaining independent degrees of freedom are

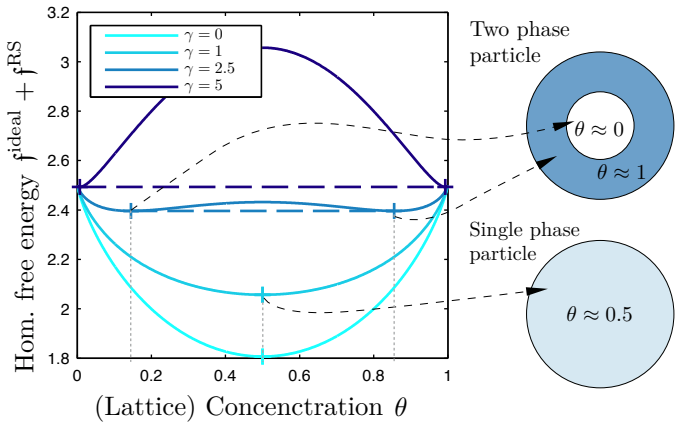

Figure 3.3.: (Left) Homogenous free energy density $\mathfrak{f}^{\text{ideal}} + \mathfrak{f}^{\text{RS}}$ as function of the intercalated (normalized) ion concentration θ for a regular solution model. For $\gamma = 0$ the hom. free energy has a minimum at $\theta = 0.5$, which leads to a single phase (lower right). In contrast, for $\gamma = 3.5$, the hom. free energy density has two local minima, resulting in a phase separation (upper right). Reprint from fig. 3 in [44].

(T, θ), where

$$\theta = \frac{n_C}{n_\ell} \tag{3.53}$$

refers to the amount or coverage of intercalated cations, *i.e.* lithium. Since lithiums ion intercalate into an electrode via the reaction $\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li}$, the intercalated lithium is uncharged. In the case of a phase separating material with two preferred phases, *i.e.* a non-ideal mixing behavior, an energy contribution $\mathfrak{f}^{\text{RS}}$ for a regular solution is added[29]. Phase separation within a particle generates a phase boundary, which could either be diffuse or sharp, and its interfacial free energy has to be explicitly taken into account [60, 121] as additional free energy contribution $\mathfrak{f}^{\text{PB}}$. The free energy density is then based on a solid electrolyte (with uncharged species), and according to section 2.10.2

$$\mathfrak{f} = \mathfrak{f}^{\text{ideal}} + \mathfrak{f}^{RS} + \mathfrak{f}^{\text{PB}} \tag{3.54}$$

where

$$\mathfrak{f}^{\text{ideal}}(T, n_\ell, \theta) = n_\ell \cdot \left(\psi_I^{\text{R}} \cdot \theta_\alpha + T^2 \cdot C_T + k_{\text{B}} T \, \theta \cdot \ln\left(\frac{\theta}{\theta_V}\right)\right) \tag{3.55}$$

$$\mathfrak{f}^{\text{RS}}(T, n_\ell, \theta) = n_\ell k_{\text{B}} T \, \gamma \cdot (\theta \cdot \theta_V). \tag{3.56}$$

Free energy contributions due to a regular solution can also be translated into activity coefficients $\gamma_k^{\text{RS}} = \exp(-\alpha\theta)$. The free energy contribution due to the phase boundaries are essentially proportional to the gradient of θ[42, 43] (interfacial free energy) and hence

$$g^{\text{PB}}(T, n_\ell, \nabla\theta) = \frac{1}{2} n_\ell \cdot \gamma^{\text{PB}} (\nabla\theta)^2. \tag{3.57}$$

The term g^{PB} is also sometimes called *gradient penalty term*[60] since the phase boundary drains energy from the system, and the sum $\mathfrak{f}^{\text{ideal}} + \mathfrak{f}^{RS}$ is called homogenous free energy

(*c.f.* figure 3.3). However, since the material function of the free energy is now also dependent on $\nabla\theta$, the definition of the chemical potential has to be adopted. The overall free energy

$$F = \int_{\Omega} \mathfrak{f}(T, \theta, \nabla\theta)\, dV \tag{3.58}$$

is actually a functional of θ, *i.e.* $F = F[\theta]$. Building hence the functional derivative of $F[\theta]$ with respect to θ leads to

$$\frac{\delta F}{\delta n_I} = n_\ell^{-1} \frac{\partial \mathfrak{f}}{\partial c_I} - n_\ell^{-1} \operatorname{div} \frac{\partial \mathfrak{f}}{\partial \nabla c_I}, \tag{3.59}$$

which is then interpreted as the chemical potential (in the case of a constant n_ℓ), *i.e.*

$$\overline{\mu}(T, \theta, \nabla\theta) = n_\ell^{-1} \cdot \frac{\partial \mathfrak{f}^{\text{ideal}}(T, n_\ell, \theta) + \mathfrak{f}^{\text{RS}}(T, n_\ell, \theta)}{\partial \theta} - \operatorname{div} \gamma^{\text{PB}} \nabla\theta \tag{3.60}$$

$$= \psi_{Li}^{R} + k_{\text{B}} T \ln\left(\frac{\theta}{1-\theta}\right) + k_{\text{B}} T\, \gamma \cdot (1 - 2 \cdot \theta) - \operatorname{div} \gamma^{\text{PB}} \nabla\theta. \tag{3.61}$$

Note that elastic strain may also significantly contribute to the chemical potential[122].

In the **isothermal** case the remaining balance equation system is

$$n_\ell \frac{\partial \theta}{\partial t} = -\operatorname{div} \bar{\mathbf{j}} \tag{3.62}$$

$$\bar{\mathbf{j}} = \mathbf{L} \cdot \nabla \overline{\mu} \tag{3.63}$$

with a positive definite Onsager coefficient $\mathbf{L}$. Relating the mobility $\mathbf{L}$ to a diffusion tensor $\mathbf{D}$ via $k_{\text{B}} T\, \mathbf{L} = \theta \cdot \mathbf{D}$ [123] leads to the Cahn–Hilliard equation

$$\frac{\partial \theta}{\partial t} = \operatorname{div} \mathbf{D} \cdot \left(\left(\frac{1}{1-c} - 2\gamma\, \theta \right) \nabla\theta - \theta \cdot \nabla^2 \left(\gamma^{\text{PB}} \nabla\theta \right) \right). \tag{3.64}$$

Corresponding boundary conditions modeling the intercalation reaction with Cahn–Hilliard type equations can be found in [121]. Numerical simulations of Cahn–Hilliard equations are widely used to investigate the behavior of phase separating materials with respect to their shape, size and velocity of charging[60, 65, 120, 124].

3.3.2 Open circuit potential

If a single electrode particle is in contact with a lithium reference electrode via an external wire, and internally connected through the electrolyte, an open circuit potential is measured with a high-ohmic voltmeter (*i.e.* negligible current). Consider thus an anode Ω_A, an electrolyte phase Ω_E and a cathode Ω_C. The anode/electrolyte interface is $\Sigma_A = \Omega_A \cup \Omega_E$ and the electrolyte/cathode interface is $\Sigma_C = \Omega_C \cup \Omega_E$. At each electrode/-electrolyte interface an electrochemical reaction $\mathrm{C}^+ + \mathrm{e}^- \rightleftharpoons \mathrm{C}$ occurs and is assumed to be in equilibrium for the moment. Note that such an equilibrium is established if the anode and the cathode are **not** connected via an external cable, *i.e.* if **no current is flowing**, or with a high-ohmic resistor in between. Let $\underset{\text{a}}{\overline{\mu}_\alpha}$ denote the chemical potential of species α on the singular surface Σ_A and $\underset{\text{c}}{\overline{\mu}_\alpha}$ the surface chemical potential on Σ_C. The

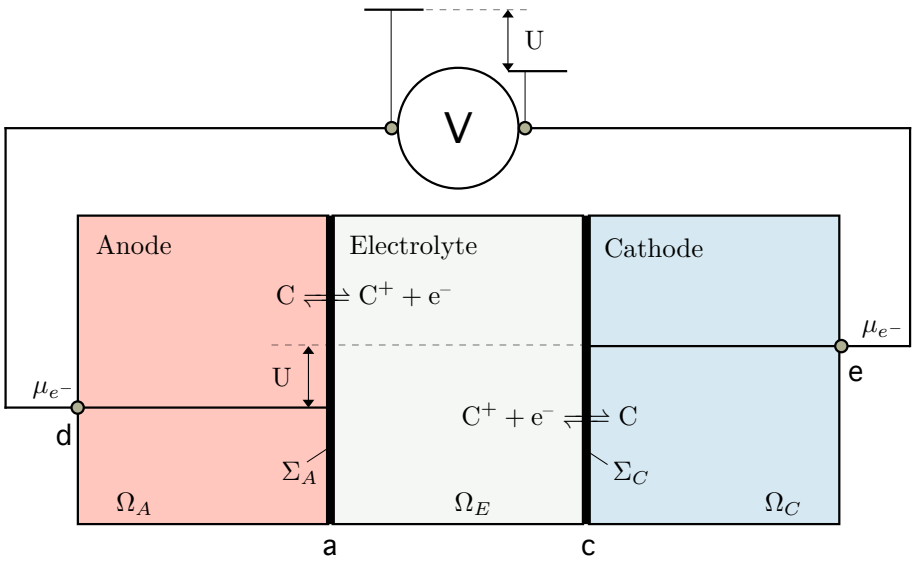

Figure 3.4.: Sketch of an anode|electrolyte|cathode setup with interfaces Σ_A and Σ_C. The actual potential difference U between the anode and the cathode could be measured with a very high ohmic voltmeter to ensure the equilibrium conditions.

equilibrium condition for surface reactions (2.313) is hence

$$\underset{\mathrm{a}}{\overline{\mu}}_{C^+} + \underset{\mathrm{a}}{\overline{\mu}}_{e^-} = \underset{\mathrm{a}}{\overline{\mu}}_{C} \qquad \text{on } \Sigma_A \tag{3.65}$$

$$\underset{\mathrm{c}}{\overline{\mu}}_{C^+} + \underset{\mathrm{c}}{\overline{\mu}}_{e^-} = \underset{\mathrm{c}}{\overline{\mu}}_{C} \qquad \text{on } \Sigma_C. \tag{3.66}$$

Further, let $\overline{\mu}_\alpha(\mathbf{x}), \mathbf{x} \in \Sigma_A$ be denoted by $\overline{\mu}_\alpha\big|_A$ and similar $\overline{\mu}_\alpha\big|_C$ for the **volumetric** chemical potential, evaluated at the respective boundary. The flux equilibrium condition (*c.f.* section 2.10.1) states

$$(\overline{\mu}_{C^+} - \overline{\mu}_S)\big|_a = (\overline{\mu}_{C^+} - \overline{\mu}_S)\big|_c + e_0 z_C\, U, \tag{3.67}$$

where U is the whole electrostatic potential difference in the electrolyte phase. If the solvent **does not adsorb** on the electrode surface Σ_A and Σ_C[6], *i.e.* there is no surface species density $\underset{\mathrm{s}}{n}_S$, the surface chemical potentials vanish, *i.e.*

$$\underset{\mathrm{a}}{\overline{\mu}}_S = 0 \qquad \text{and} \qquad \underset{\mathrm{c}}{\overline{\mu}}_S = 0. \tag{3.68}$$

The continuity condition of the chemical potential (*c.f.* corollary 7) thus implies

$$\overline{\mu}_S\big|_a = 0 \qquad \text{and} \qquad \overline{\mu}_S\big|_c = 0 \tag{3.69}$$

and hence

$$\overline{\mu}_{C^+}\big|_a = \overline{\mu}_{C^+}\big|_c + e_0 z_C\, U. \tag{3.70}$$

If the electrodes are **ideal conductors**, *i.e.* $n^{\mathrm{F}} = 0$ in Ω_A and Ω_C, one could employ

[6] An in-depth investigation of this assumption is part of my current research work.

the flux equilibrium condition also on the electrons, *i.e.*

$$\underset{\mathrm{a}}{\overline{\mu}_{e^-}} = \overline{\mu}_{e^-}|_d \tag{3.71}$$

$$\underset{\mathrm{c}}{\overline{\mu}_{e^-}} = \overline{\mu}_{e^-}|_e, \tag{3.72}$$

where d denotes some bulk point the anode and e a bulk point in the cathode, and (fairly) assume that the chemical potential of the electrons is constant in the bulk.
For the introduction of the open circuit potential it is further sufficient to assume that the species C are homogeneously distributed in the (reference) electrode[7] Ω_C, which implies

$$\overline{\mu}_C\big|_c = \overline{\mu}_C\big|_d = \text{const.} \tag{3.73}$$

Last but not least, the continuity condition of $\underset{\mathrm{a}}{\overline{\mu}_C}$ implies

$$\underset{\mathrm{a}}{\overline{\mu}_C} = \overline{\mu}_C\big|_a = \overline{\mu}_C(\mathbf{x}), \quad \mathbf{x} \in \Sigma_A \tag{3.74}$$

Note, however, that for an intercalation electrode $\overline{\mu}_C(\mathbf{x})$, $\mathbf{x} \in \Sigma_A$ is actually a function of the concentration θ, evaluated **at** the interface Σ_A, *i.e.*

$$\overline{\mu}_C\big|_a = \overline{\mu}_C(\theta|_a). \tag{3.75}$$

Overall one thus obtains

$$U = \frac{1}{e_0 z_C} \cdot \left(\underset{\mathrm{a}}{\overline{\mu}_C} - \overline{\mu}_C\big|_D - \overline{\mu}_{e^-}\big|_E + \overline{\mu}_{e^-}\big|_D \right). \tag{3.76}$$

The constant expression $\overline{\mu}_C|_D - \overline{\mu}_{e^-}|_E + \overline{\mu}_{e^-}|_D$ is quite often abbreviated as $\overline{\mu}_C^{\mathrm{R}}$, leading to the *simple* expression

$$U = \frac{1}{e_0 z_C} \cdot \left(\overline{\mu}_C(\theta|_a) - \overline{\mu}_C^{\mathrm{R}} \right), \tag{3.77}$$

which corresponds to the general Nernst equation for intercalation reactions in the working electrode.

Auxiliary calculation 3.45:

$$\begin{aligned}
\underset{\mathrm{a}}{\overline{\mu}_C} &= \underset{\mathrm{a}}{\overline{\mu}_{C^+}} + \underset{\mathrm{a}}{\overline{\mu}_{e^-}} = \mu_{C^+}\big|_C + e_0 z_C \cdot U + \underset{\mathrm{a}}{\overline{\mu}_{e^-}} \\
&= \underset{\mathrm{c}}{\overline{\mu}_C} - \overline{\mu}_{e^-}\big|_D + U + \overline{\mu}_{e^-}\big|_E \\
&= \overline{\mu}_C\big|_D - \overline{\mu}_{e^-}\big|_D + U + \overline{\mu}_{e^-}\big|_E
\end{aligned}$$

To measure the open circuit potential of an electrochemical cell, one would apply a very high ohmic voltmeter between the anode and the cathode, to ensure the no-flux equilibrium condition.

[7] Consider a metallic lithium reference electrode, which is, of course, homogeneously *made* of metallic lithium.

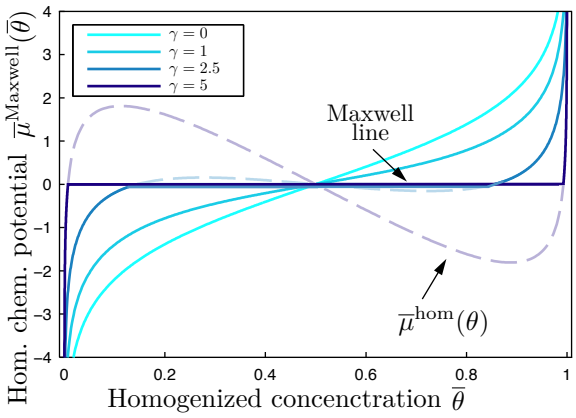

Figure 3.5.: Cell potential obtained from the homogenization of chemical potential with a Maxwell construction. The non-monotone chemical potential $\overline{\mu}^{\text{hom}}(\theta)$ (transparent) is *corrected* to obtain the homogenized chemical potential $\overline{\mu}^{\text{Maxwell}}(\overline{\theta})$ for different phase separation parameters γ. Reprinted from fig. 4 in [44]

However, from a theoretical point of view one desires an explicit relationship between the cell potential and the concentration or amount of intercalated lithium, *i.e.* $U = U(\theta\big|_a)$. One has therefore to solve equation (3.64) for the constraints

$$\frac{1}{\text{vol}\{\Omega_A\}} \int_{\Omega_A} \theta(\mathbf{x}, t)\, dV = \overline{\theta} \qquad \overline{\theta} \in [0, 1], \tag{3.78}$$

where $\overline{\theta}$ is the prescribed amount of intercalated lithium. This is the *full approach* to determine the cell potential of a phase separating single particle.

In a phase separating material, the chemical potential at the interface Σ_A is not equal to the chemical potential in the bulk. However, one could also ask for an approximated relationship between the cell potential U and the averaged (or homogenized) concentration

$$\overline{\theta} = \frac{1}{\text{vol}\{\Omega_A\}} \int\limits_{\Omega_A} \theta\, dV \tag{3.79}$$

for which $\overline{\theta}(\mathbf{x}) = \overline{\theta}$ (*i.e.* independent of the position $\mathbf{x}$) and thus $\theta\big|_a = \overline{\theta}$. To deduce such a relationship, the *homogenous* part of the chemical potential

$$\overline{\mu}^{\text{hom}}(\theta) = \psi_{Li}^{R} + k_{\text{B}} T \ln\left(\frac{\theta}{1-\theta}\right) + k_{\text{B}} T\, \gamma \cdot (1 - 2 \cdot \theta) \tag{3.80}$$

is corrected with the Maxwell construction[125]. This is done by connecting the two minima in the free energy, if present, by a straight line and *substitute* the non-montonic part of the free energy with it (cf. figure 3.3). The thereby obtained chemical potential $\overline{\mu}^{\text{Maxwell}}(\overline{\theta})$ is then a homogenous equivalent to the actual 2-phase system $\overline{\mu}^{\text{hom}}(\theta)$ and enables thus the definition of a cell potential

$$U(\overline{\theta}) = \frac{1}{z_C e_0} (\overline{\mu}^{\text{Maxwell}}(\overline{\theta}) - \overline{\mu}_C^{\text{R}}). \tag{3.81}$$

3.3.3 Many particle electrode

Similar to above, the counter electrode (or cathode) is a homogenous, non-phase separating reference electrode. However the anode[8] consists of N (N is typically in the order of 10^9 [2]) particles and the open circuit potential with respect to the reference electrode is desired. It is clear that a full resolution of each particle is far to complicated to be ever computable with a finite amount of computational time. Hence, homogenization strategies are desired to derive some general expression of the open circuit potential of a many particle electrode.

In the overall equilibrium situation, *i.e.* flux and reaction equilibrium, even the electrode surface, one could again derive some general relationships on the open circuit potential. [9] Since all the anode particles are interconnected via the electrolyte, the equilibrium condition requires that

$$\underset{\mathrm{a}}{\overline{\mu}_\alpha^k}[C] \overset{!}{=} \underset{\mathrm{a}}{\overline{\mu}_C^\ell} \qquad k, \ell = 1, \ldots, N, \tag{3.84}$$

where $\underset{\mathrm{a}}{\overline{\mu}_\alpha^k}$ is the surface chemical potential of the cations on particle k. Due to the continuity of the chemical potential, and with equivalent material function for all particles, one could also write

$$\overline{\mu}_C(\theta_k\big|_a) \overset{!}{=} \overline{\mu}_C(\theta_\ell\big|_a) \qquad k, \ell = 1, \ldots, N \tag{3.85}$$

where $\theta_k\big|_a$ is now the concentration of intercalated ions in particle k, evaluated at the respective interface. Choosing one particle as a reference, *e.g.*

$$\overline{\mu}_{\mathrm{Many}}(\theta\big|_a) := \overline{\mu}_C(\theta_1\big|_a), \tag{3.86}$$

allows one to express the open circuit potential of a many particle electrode as

$$U = \frac{1}{e_0 z_C}\left(\overline{\mu}_{\mathrm{Many}}(\theta\big|_a) - \overline{\mu}^{\mathrm{R}}\right). \tag{3.87}$$

While for a single particle the assumption of a homogenous distribution of intercalated Li in a phase separating material is not feasible or has to be corrected via the Maxwell construction, assuming a homogenous distribution in a many particle system is, to some extend, valid [120].

For an electrode which consist of two particles, let θ_1 be the homogenous concentration of intercalated lithium in particle 1 and θ_2 in particle 2. A homogenous equilibrium state

[8] Note that terms anode and cathode are used here quite arbitrary as the they *change* whether one charges or discharges a cell. It is just used to distinguish electrode Ω_A and electrode Ω_C.

[9] Note that the flux equilibrium state is actually independent of the geometry of the porous electrode. Recall the flux equilibrium condition

$$\nabla \frac{\overline{\mu}_{C^+} - \overline{\mu}_S}{T} - e_0 z_C \nabla \Phi = \mathbf{0} \tag{3.82}$$

which was integrated via some path integral over a curve Ψ. Here, the initial point of the path integration is $\mathbf{x}_C$, $\mathbf{x}_C \in \Sigma_C$ and as long as**any** path Ψ could be found between a point $\mathbf{x}_C$ and a point $\mathbf{x}_A$ on Σ_A, one obtains the simple relationship

$$e_0 z_C U = (\overline{\mu}_{C^+} - \overline{\mu}_S)\big|_A - (\overline{\mu}_{C^+} - \overline{\mu}_S)\big|_C. \tag{3.83}$$

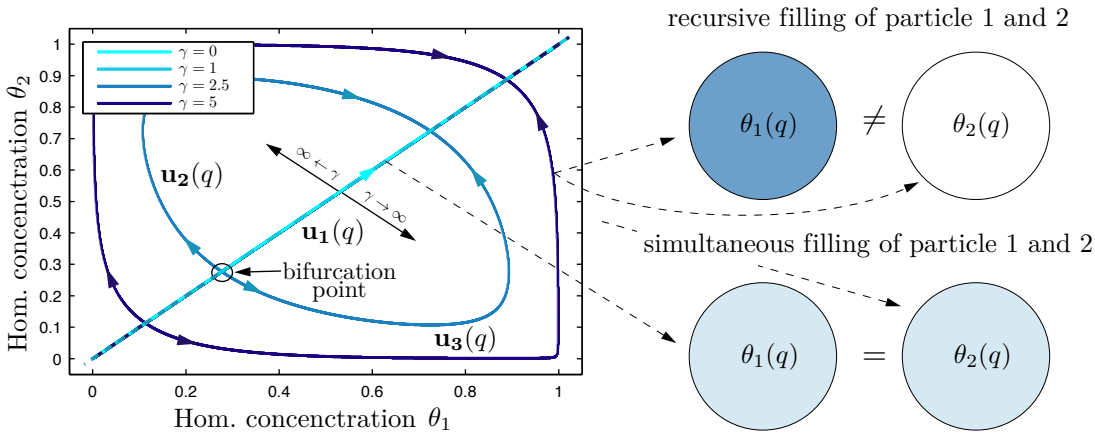

Figure 3.6.: Sketch of the homogenous concentration θ_1 in particle 1 and θ_2 in particle 2 as parametric curves $\mathbf{u} = (\theta_1(q), \theta_2(q))$, *i.e.* solutions of equation 3.85 for $N = 2$. For $\gamma > 2$ bifurcation points occurs at which equation (3.90) spontaneously possesses new solutions $\mathbf{u_1}, \mathbf{u_2}$ and $\mathbf{u_3}$.

exits, **if** the condition (3.85) **has solutions** $(\theta_1(q), \theta_2(q))$ for a parameter $q \in [0, 1]$ with

$$(\theta_1(0), \theta_2(0)) = (0, 0) \tag{3.88}$$
$$(\theta_1(1), \theta_2(1)) = (1, 1). \tag{3.89}$$

Condition (3.85) implies an implicit curve

$$\ln\left(\frac{\theta_1}{1-\theta_1} \cdot \frac{1-\theta_2}{\theta_2}\right) + 2\gamma \cdot (\theta_2 - \theta_1) \overset{!}{=} 0, \tag{3.90}$$

which indeed has parametric solutions (curves) $\mathbf{u_m}(q) = (\theta_1(q), \theta_2(q))_\mathbf{m} \in \mathbb{R}^2$ ($\mathbf{m}$ is the solution index) and the parameter q is, similar to the single electrode, the status of charge. For $\gamma < 2$, the equation system has one solution, $\theta_1(q) = \theta_1(q) = 1/2 \cdot q$, which corresponds to an equal filling degree of the two particles. However, for $\gamma > 2$ bifurcation points occur at which the equation system spontaneously has two additional solutions (cf. figure 3.6). Note that for $\gamma > 2$ the symmetric solution $\theta_1 = \theta_2$ is **not** anymore a minimum of the free energy, but a local maximum[126] since the Hessian is negative definite for this solution. Hence, for $\gamma > 2$, the preferable distribution of intercalated ions, in the equilibrium situation, is not an equal filling of both particles but a subsequent filling of particle 1, followed by particle 2 (or the other way round).

According to equation (3.87) the cell potential of such a two particle electrode is equal to the chemical potential μ as function of $\theta_1(q)$ (or $\theta_2(q)$). In figure 3.7 the chemical potential (and thus the cell potential as $\overline{\mu}^{\mathrm{R}} = \text{const.}$) for a two particle electrode is displayed.

In a many particle electrode the overall amount of intercalated ions (or macroscopic filling degree, status of charge) q of a many particle electrode is

$$q = \frac{1}{N} \sum_{k=1}^{N} \frac{1}{\mathrm{Vol}(\Omega_k)} \int_{\Omega_k} \theta_k d\mathbf{x} \overset{\text{local eq.}}{=} \frac{1}{N} \sum_{k=1}^{N_A} \theta_k. \tag{3.91}$$

Similar to the two particle system a set of solutions $(\theta_1(q), \ldots, c\theta_(q))_\mathbf{m}$ for a given value of q exists, fulfilling the equation system (3.84) in addition to a positive definite Hessian

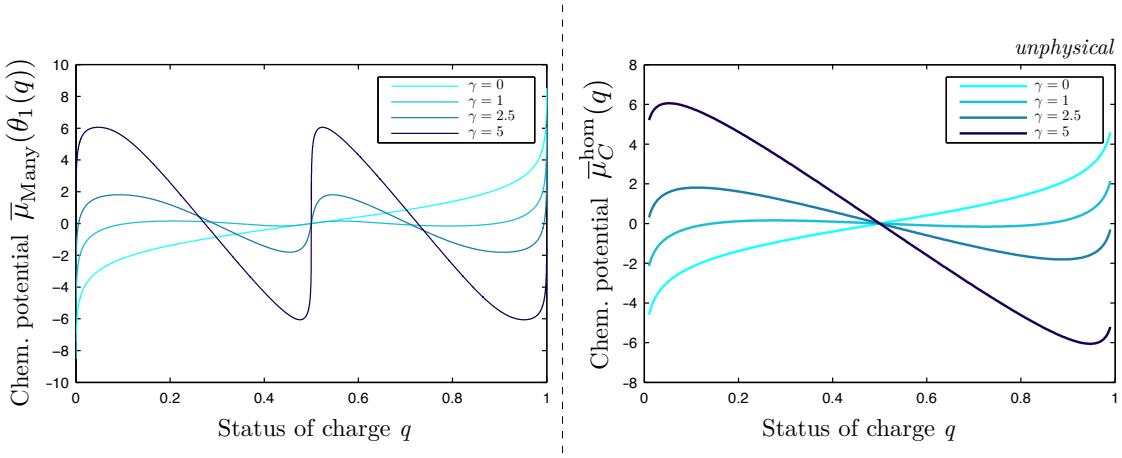

Figure 3.7.: (Left) Cell potential of a two particle electrode as function of the status of charge q. While for the non-phase separating solution $c_{\mathbf{1}}^1$ the classical single particle potential is obtained, oscillations of the cell potential occur due to the recursive filling of particle 1 and 2. (Right) For comparison reasons the *unphysical* homogenous chemical potential of a single particle is displayed.

of G with respect to θ_k. Extended studies of this kind, incorporating statistical methods to treat a huge amount of particles, have been performed by Dreyer *et al.*[2, 126, 127] in which the inter-particle phase separation has been identified as the origin the cell potential hysteresis in $LiFePO_4$ electrodes.

Of course, a two particle system as well as a resolution of N particles explicitly is not appropriate for larger scale applications of mathematical modeling. To investigate the non-equilibrium behavior of a many particle electrode, and thus account for the kinetics of the intercalation reaction, field averaging strategies are used to derive homogenized (macroscopic) PDEs.

3.4 Porous electrode theory

Porous electrode theory, initially invented by Newman *et. al.* [51, 55], is frequently used in modeling porous electrodes of either batteries or fuel cells. Its basic idea is to average the microscopic field variables in a *representative volume element* (REV) and treat the surface reactions as volumetric sink term[128]. In the electrolyte phase electroneutrality is assumed, which thus allows for a homogenization of the porous medium. Since only simple diffusion equations are mainly used for the intercalation material, an actual prediction of the open circuit potential (as function of some global status of charge q) fails. This circumstance is corrected with the introduction of a fit parameter $U^{\text{fit}}(q)$ in order to reproduce the open circuit potential of the desired cell[106, 129]. However, a self consistent incorporation of the open circuit potential in porous electrode theory is at its very begging [130] and this work is also step towards a more rigorous porous electrode theory.

Before actually deriving the homogenized equations, a brief introduction on averaging field properties is given. The integral mean of a field variable Ψ_i with respect to its specific

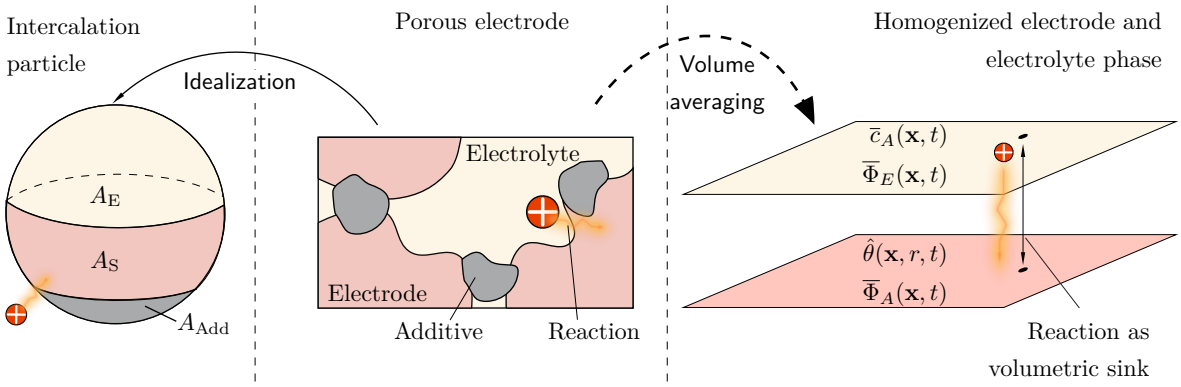

Figure 3.8.: (Middle) Representative volume element (REV) of the three phase system electrode, electrolyte and conductivity additive. An idealized ball shaped particle (left) determines the surface area in contact with another electrode particle (A_S), with electrolyte (A_E) and with the additive A_{Add}. The volume averaging procedure generates two superimposed continua, the macroscopic electrolyte and electrode phase (right). Electrochemical reactions occurring at the electrode/electrolyte interface are translated into volumetric sink terms. Modified reprint from [44].

volume Element Ω_i is

$$\overline{\Psi}_i := \frac{1}{V_i}\int\limits_{\Omega_i} \Psi(\mathbf{x},t)\,dV = \frac{\varepsilon_i}{V}\int\limits_{\Omega_i} \Psi(\mathbf{x},t)\,dV, \tag{3.92}$$

where V is the volume of the REV Ω, V_i the volume and $\varepsilon_i = V_i/V$ is the porosity of phase i. If Ω is arbitrary one can shrink the volume element to its volumetric center $\mathbf{r}$, and use $\mathbf{r}$ as macroscopic space coordinate. The partial time derivate, assuming that the geometry remains constant in time, is

$$\overline{\frac{\partial \Psi_i}{\partial t}} = \varepsilon_i \frac{\partial \overline{\Psi}_i}{\partial t}. \tag{3.93}$$

and the averaged gradient of a scalar field is

$$\overline{\nabla \Psi_i} = \nabla \overline{\Psi}_i + \frac{1}{V}\int\limits_{\partial\Omega_i} \Psi\,dA. \tag{3.94}$$

To account for variations of the macroscopic field variables due to the microscopic flux from one phase to another, e.g. electrochemical reactions, the flux equations are averaged. For a general flux $\mathbf{j}$, the averaged divergence is

$$\overline{\nabla \cdot \mathbf{j}} = \nabla \cdot \overline{\mathbf{j}} + \frac{1}{V}\int\limits_{\partial\Omega_i} \mathbf{j} \cdot\, d\mathbf{A}. \tag{3.95}$$

Note the additional flux term through the interface between the two phases.[44]

3.4.1 Electrolyte phase

This averaging scheme is applied to the transport equations derived in section 3.2 and 3.3, starting with the electrolyte phase. The flux (or electric current) through the surface Σ_A is essentially determined by the intercalation reactions $\mathrm{C}^+ + \mathrm{e}^- \rightleftharpoons \mathrm{C}$ (*c.f.* section 3.3.2). It is assumed that only cations contribute to the electrochemical reaction, *i.e.* that there is no oxidation of the anion[10]. If the cations are *produced* with a given source rate $\underset{\mathrm{s}}{r}_C$ and the anions conserved, the fluxes through the interface are

$$\frac{1}{V}\int\limits_{\partial\Omega_E} \mathbf{j}_C \cdot d\mathbf{A}, = \frac{1}{V}\int\limits_{\partial\Omega_E} \underset{\mathrm{s}}{r}_C \; dA \tag{3.96}$$

$$\frac{1}{V}\int\limits_{\Omega_i} \mathbf{j}_A \cdot \mathbf{n}\, d\mathbf{A} = 0. \tag{3.97}$$

Since the additive material is assumed to be chemically non active, reactions only occur along $\partial\Omega_E$ with a surface area A_E. Assuming that the reaction occurs homogenous along $\partial\Omega_E$ one is able to write

$$\frac{1}{V}\int\limits_{\partial\Omega_E} \mathbf{n}\cdot\mathbf{j}_C = \frac{A_E}{V}\cdot \underset{\mathrm{s}}{q}_C := a_E \cdot \underset{\mathrm{s}}{r}_C, \tag{3.98}$$

where a_E is the specific (or reactive) surface area between the electrode and the electrolyte phase.

Next I assume a *strong* electroneutrality within the electrolyte and use the results from section 3.2. For the overall current through the electrolyte, the averaged charge conservation equation is

$$0 = \overline{\nabla\cdot\mathbf{j}^{\mathrm{F}}} = \nabla\cdot\overline{\mathbf{j}^{\mathrm{F}}} + e_0 z_C a_E \cdot \underset{\mathrm{s}}{r}^A_{C^+}, \tag{3.99}$$

where the index A refers to the averaging in the domain $\overline{\Omega}_A$. Insertion of equation (3.50) leads to the generalized ohmic law for the electrolyte,

$$-\mathrm{div}\left(\kappa_\vartheta \nabla\frac{1}{\overline{T}} + \kappa_F \nabla\widetilde{\Phi} + t_A\cdot\kappa_F \frac{\partial\,\widetilde{\mu}(\overline{c_A})}{\partial\,\overline{c_A}}\nabla\overline{c_A}\right) = e_0 z_C a_E \cdot \underset{\mathrm{s}}{r}^A_{C^+}. \tag{3.100}$$

Since the anions are non-reactive they obey an averaged conservation equation

$$\frac{\partial\overline{c_A}}{\partial t} = \overline{\nabla\cdot\mathbf{j}_A} = \nabla\cdot\overline{\mathbf{j}_A}. \tag{3.101}$$

With eq. (3.51) the averaged diffusion equation for the anions is obtained

$$\frac{\partial\,\partial\overline{c_A}}{\partial\,t} = \mathrm{div}\left((\gamma_\vartheta - t_A\cdot\kappa_\vartheta)\cdot\nabla\frac{1}{\overline{T}} + \overline{D_A}\nabla\overline{c_A}\right). \tag{3.102}$$

The averaged diffusion coefficient $\overline{D_A}$ is, however, difficult to obtain. An estimation of averaged diffusion coefficients is a huge topic, and I refer to the literature for an in-depth investigation, *e.g.* [55, 128, 131–134].

[10] However, with the framework of chapter 2 an incorporation of anion oxidation is of course possible.

3.4.2 Electrode phase

Intercalation in the porous electrode is now modeled with averaged transport equations for the electrode regime. Exemplarily the derivation is performed for the porous anode and the electrode index ^{I} is dropped. To treat the particle intercalation spatially resolved, even on the micro scale, I assume that each electrode particle Ω_A^k is a ball B with radius r_A and center $\mathbf{x}_k$. The particles are assumed to be in contact with other electrode particles through the surface S_{AA} and with the electrolyte through $S_{AE} = \partial\Omega_E$. As in the previous section, it is assumed that the electrode consists of N single particles, and one can write the overall concentration field[11]

$$\hat{\theta} = \hat{\theta}(\mathbf{x}, \mathbf{r}) = \sum_{k=1}^{N} \theta_k(\mathbf{r}, t) \cdot \chi_B(\mathbf{x} - \mathbf{x}_k). \tag{3.103}$$

In the limit of infinitely many particles, the summation becomes

$$\hat{\theta}(\mathbf{x}, \mathbf{r}) = \int_{\mathbb{R}^3} \theta(\mathbf{x}, \mathbf{y}).\delta(\mathbf{r} - \mathbf{y})\, dV. \tag{3.104}$$

The field variable $\hat{\theta}$ is dependent on the microscopic space coordinate $\mathbf{r}$ *and* the macroscopic coordinate $\mathbf{x}$, and consequently called **micro-macro concentration**. Since both scales are resolved, the concentration is a conserved quantity and thus obeys a conservation equation

$$\frac{\partial \hat{\theta}}{\partial t} = -\mathrm{div}_{\mathbf{r}} \cdot \mathbf{j}_{\mathrm{Mic}} - \mathrm{div}_{\mathbf{x}} \cdot \mathbf{j}_{\mathrm{Mac}}, \tag{3.105}$$

where $\mathrm{div}_{\mathbf{r}}$ denotes the microscopic divergence[12] and $\mathrm{div}_{\mathbf{x}}$ the macroscopic divergence.

The interpretation of this equation is the following:

- The scalar field $\hat{\theta} = \hat{\theta}(\mathbf{x}, \mathbf{r})$ incorporates microscopic concentration gradients $\nabla_{\mathbf{r}}\hat{\theta}(\mathbf{x}, \mathbf{r})$ within a particle *and* macroscopic variations between particles, $\nabla_{\mathbf{x}}\hat{\theta}(\mathbf{x}, \mathbf{r})$.
- The Microscopic flux $\mathbf{j}_{\mathrm{Mic}}$ corresponds to the flow within a particle.
- $\int_{S_{AE}} \mathbf{j}_I \cdot d\mathbf{A}$ quantifies the flux of ions into the electrode due to the intercalation reaction and corresponds thus to the flux boundary condition of $\mathbf{j}_{\mathrm{Mic}}$ at the particle surface $r = r_A$.
- Ion flux from one electrode particle to a (connected) neighbor is interpreted as macroscopic flux, *i.e.* $\nabla_{\mathbf{x}} \cdot \mathbf{j}_{\mathrm{Mac}} = \int_{S_{AA}} \mathbf{j}_I \cdot d\mathbf{A}$ (Inter-diffusion).

It was already mentioned that the flux of lithium into the ball-shaped particles is assumed to be homogenous along the particle surface. This allows one to write the flux- or Neumann-boundary condition for the microscopic flux as

$$\mathbf{n}_{\mathbf{r}} \cdot \mathbf{j}_{\mathrm{Mic}} = a_E \cdot \underset{\mathrm{s}}{r_C^I}(\hat{\theta}, \overline{c_A}, \overline{\Phi}_A, \overline{\Phi}_E) \text{ on } \mathbf{r} = r_A. \tag{3.106}$$

[11] $\chi_B(\mathbf{r})$ is the indicator function:

$$\chi_B(\mathbf{r}) = \begin{cases} 1, & \text{if } ||\mathbf{r}|| < r_E \\ 0, & \text{else} \end{cases}$$

[12] Since the microscopic particle is assumed to be ball shaped, the operators div_r and ∇_r are to be understood in spherical coordinates.

The explicit representation of $\underset{\mathrm{s}}{r}{}^{I}_{C}(\hat{\theta}, \overline{c_A}, \overline{\Phi}_A, \overline{\Phi}_E)$ is given in section 3.5.

Regarding an inter-particle flux diffusion I just mention here that most modeling approaches neglected the interdiffusion on the macro scale. In numerical implementations is is used as a stabilization mechanism [135], however, without any physical meaning. For a comparison to a full 3-D electrode model this effect in porous electrode theory could be crucial, since intercalated lithium could of course diffuse in the electrode network. A first step is hence to assume a macroscopic interdiffusion of classical Fickian type, *i.e.*

$$\mathbf{j}_{\mathrm{Mac}} = -D_{\mathrm{Inter}} \nabla_{\mathbf{x}} \hat{\theta}(\mathbf{x}, \mathbf{r}), \tag{3.107}$$

where D_{Inter} is a measure how well the electrode particles are connected to each other. Such a connection could either be direct[13] or through some filler material[14].

The microscopic diffusion $\nabla_{\mathbf{r}} \cdot \mathbf{j}_{\mathrm{Mic}}$ could be described with the model derived in section 3.3.1, e.g. the Cahn–Hilliard-type equation (3.64). However, incorporation of phase separation equations in porous electrode theory are at its very beginning, with a first publication of T. R. Ferguson and M. Z. Bazant in October 2012 [130]. In contrast, *simple* microscopic diffusion $\mathbf{j}_{\mathrm{Mic}} = D_{\mathrm{Inner}} \nabla_{\mathbf{r}} \hat{\theta}$ is assumed in most modeling approaches[3, 55, 97, 101–103].

Applying thus the model derivations of section 3.3.1 leads to a general balance equation for the micro-macro concentration $\hat{\theta}(\mathbf{x}, r, t)$. According to eq. 3.62 and eq. 3.105 one obtains

$$\frac{\partial \hat{\theta}(\mathbf{x}, r, t)}{\partial t} = \nabla_{\mathbf{r}} \cdot \mathbf{L} \nabla_{\mathbf{r}} \overline{\mu}_C(\hat{\theta}) + \nabla_{\mathbf{x}} \cdot D_{\mathrm{Inter}} \nabla_{\mathbf{x}} \hat{\theta} \tag{3.108}$$

where $\overline{\mu}_C$ is the material function of the microscopic electrode phase. Note that $\mathbf{L}$ is not an averaged Onsager coefficient but the microscopic mobility in radial direction. For an ideal mixture on a lattice one has the material function

$$\overline{\mu}_C(\hat{\theta}) = \psi^{\mathrm{R}} + k_{\mathrm{B}} T \ln \left(\frac{\hat{\theta}}{1 - \hat{\theta}} \right) \tag{3.109}$$

and consequently

$$\frac{\partial \hat{\theta}(\mathbf{x}, r, t)}{\partial t} = \nabla_{\mathbf{r}} \cdot \left(\mathbf{L} k_{\mathrm{B}} T \, \frac{1 - \hat{\theta}}{\hat{\theta}} \nabla_r \hat{\theta}(\mathbf{x}, r, t) \right) + \nabla_{\mathbf{x}} \cdot D_{\mathrm{Inter}} \nabla_{\mathbf{x}} \hat{\theta}(\mathbf{x}, r, t). \tag{3.110}$$

Applying the basic relationship for the mobility $k_{\mathrm{B}} T \, \mathbf{L} = D_\theta \cdot \theta$ [123], where D_θ denotes a constant diffusion coefficient, one obtains finally

$$\frac{\partial \hat{\theta}(\mathbf{x}, r, t)}{\partial t} = \nabla_{\mathbf{r}} \cdot \Big(D_\theta \cdot (1 - \theta) \nabla_r \hat{\theta}(\mathbf{x}, r, t) \Big) + \nabla_{\mathbf{x}} \cdot D_{\mathrm{Inter}} \nabla_{\mathbf{x}} \hat{\theta}(\mathbf{x}, r, t). \tag{3.111}$$

One could also interpret $D_\theta \cdot (1 - \theta)$ as the actual concentration dependent diffusion coefficient.

Note here that almost all porous electrode models rely on the central work of T. Fuller, M.

[13] The assumption of ball shape particles is very restrictive in reality and one could fairly consider a *bar-bell* shaped particle which would be treated as two particles in the theory. However, since the two particles are actually connected via the *bar-rod*, an intercalated lithium diffusion could of course occur.

[14] Most commonly graphite is used as filler material to actually enhance the electron conductivity in the matrix. However, graphite itself is also a lithium conductor and thus allows for an interdiffusion.

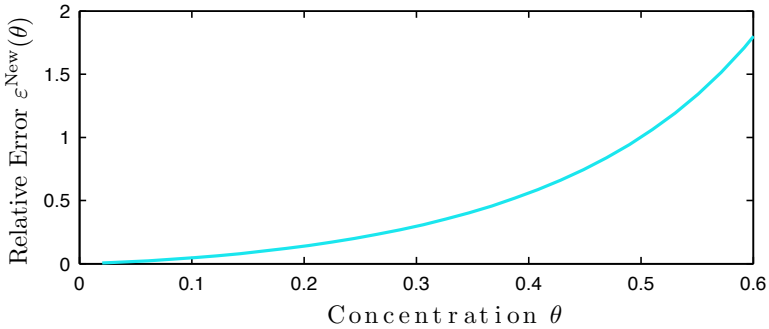

Figure 3.9.: Relative error of the open circuit potential regarding the two mixture models eq. (3.109) and eq. (3.109).

Doyle and J. Newman, "Simulation and Optimization of the Dual Lithium Ion Insertion Cell", *J. Electrochem. Soc., 1994*, **141**, 1–9, which states (in my notation) the equation

$$\frac{\partial \hat{\theta}(\mathbf{x}, r, t)}{\partial t} = \nabla_{\mathbf{r}} \cdot \left(D_\theta \nabla_r \hat{\theta}(\mathbf{x}, r, t) \right) . \tag{3.112}$$

This is in my opinion the origin of the inconsistent incorporation of the open circuit potential in the Newman model. From a thermodynamic point of view, Newman used a material function

$$\overline{\mu}_C^{\mathrm{New}} = \psi^{\mathrm{R}} + k_{\mathrm{B}} T \ln(\theta) , \tag{3.113}$$

which in equilibrium conditions implies an open circuit potential

$$U^{\mathrm{New}}(\theta) \propto \ln(\theta) . \tag{3.114}$$

An ideal mixture on a lattice, however, leads to

$$U(\theta) \propto \ln\left(\frac{\theta}{1-\theta}\right) . \tag{3.115}$$

The simple *error measure*

$$\varepsilon^{\mathrm{New}}(\theta) := \left| \frac{U^{\mathrm{New}}(\theta) - U(\theta)}{U^{\mathrm{New}}(\theta)} \right| \tag{3.116}$$

states a 100% error at $\theta = 0.5$ (*i.e.* 50% status of charge).

In that sense, I carefully state here thermodynamic inconsistency of the Newman model [3] regarding the open circuit potential. This error is *corrected* in [3] with the introduction of an additional degree of freedom $U^{\mathrm{fit}}(\theta)$. The parametric representation of $U^{\mathrm{fit}}(\theta)$ is obtained from a successive fitting of the numerical simulations (*i.e.* solutions of eq. 3.112) to experimental data. Engineering scale approaches of battery modeling and well established commercial software (e.g. Battery Design Studio[58], Comsol Multiphysics - Chemical Engineering Toolbox[135]) relay **all** on the concept of an additional fit *parameter* $U^{\mathrm{fit}}(\theta)$, in order to reproduce the open circuit potential of a measured cell. A **thermodynamic consists model**, however, is able to *predict* accurately the open circuit potential,

however, based on a (sophisticated) material function $\mathfrak{g}$. I think, with the introduction of phase separating materials in lithium ion technology (*e.g.* $LiFePO_4$ [66]), an accurate **predictability** of the open circuit potential in porous electrodes is highly desirable. In a further work I will give a an in-depth investigation of various material functions in porous electrode theory.

To close the set of equations one has to specify the macroscopic electric potential in the electrode phase. Similar to the electrolyte phase (*c.f.* eq. (3.100)), the homogenized electrode is described with an averaged excess electron density $\overline{c}^I_{e^-}$, $I = A, C$ and the averaged electrochemical potential of charge $\overline{\Phi}_I$ $I = A, C$ (*c.f.* the definition 3.32). The concept of a microscopic ion flux within an electrode particle and a macroscopic ion flux between particle is now transferred to electrons. Quite similar to the electrolyte phase (*c.f.* eq. (3.100)) an averaged electrochemical potential of charge $\overline{\Phi}_I$ $I = A, C$ (*c.f.* the definition 3.32) is introduced, for which an ohmic law is derived.

Let the excess electron density simply be the charge density n^{F}_I. An electroneutrality assumption $n^{\mathrm{F}}_I = 0$[15], which is at least in metals a quite good assumption, leads to balance equation

$$-\nabla \cdot \left(\kappa_I \nabla \overline{\Phi}_I\right) = -e_0 a_I \cdot \underset{\mathrm{s}}{r}{}^I_{e^-} \qquad I = A, C. \tag{3.117}$$

In analogy to above, the volumetric reaction rate $\underset{\mathrm{s}}{r}{}^I_{e^-}$ corresponds to the source or sink of electrons due to the the averaged surface reaction $\mathrm{Li}^+ + \mathrm{e}^- \rightleftharpoons \mathrm{Li}$ in electrode I. $\kappa_I \nabla \overline{\Phi}_I$ denotes the macroscopic averaged flux of electrons, *i.e.*

$$\mathbf{j}^I_{e^-,\mathrm{Mac}} = -\frac{1}{e_0} \kappa_I \nabla \overline{\Phi}_I. \tag{3.118}$$

Definition 12 (Porous intercalation cell)**.**

A **cell**, consisting of a porous anode, an electrolyte and a cathode is a domain $\overline{\Omega} = \overline{\Omega}_A \cup \Omega_E \cup \overline{\Omega}_C$, with $\overline{\Omega}_A \in \mathbb{R}^4$, $\Omega_E \in \mathbb{R}^3$ and $\overline{\Omega}_C \in \mathbb{R}^4$. In this four dimensional typeface $\mathbf{z} \in \overline{\Omega}_I$ and $\overline{\Omega}_I = \Omega_I \times [0, r_I]$, $I = A, C$ where the macroscopic variable $\mathbf{x}$ corresponds to $(z_1, z_2, z_3)^{\mathrm{T}}$ and the microscopic variable $r = z_4$.

The **porous anode** is described with the following physical properties:

- the averaged (electrochemical) potential $\overline{\Phi}_A(\mathbf{x})$[16] of electrons in the metal phase, obeying a generalized ohmic law eq. (3.117)
- the amount of intercalated lithium $\hat{\theta}_A(\mathbf{x}, r)$, described with the micro-macro concentration field $\hat{\theta}$ obeying a balance eq. (3.105)
- the averaged (electrochemical) potential of charge $\overline{\Phi}_E(\mathbf{x})$, satisfying eq. (3.100),
- and the anion concentration in the electrolyte phase $\overline{c_A}(\mathbf{x})$, obeying the averaged balance equation (3.102).

[15] Note that this implies that the excess charge is completely stored as surface charge, *i.e.* excess electrons.

[16] Note that in a completely four dimensional typeface $\overline{\Phi}_A = \overline{\Phi}_A(\mathbf{z})$, the last component is simply r_A, which corresponds to the electrode/electrolyte interface on the microscale, *i.e.*

$$\overline{\Phi}_A(\mathbf{x}) = \overline{\Phi}_A(\mathbf{z})\big|_{\mathbf{z}=(\mathbf{x}, r_A)} \tag{3.119}$$

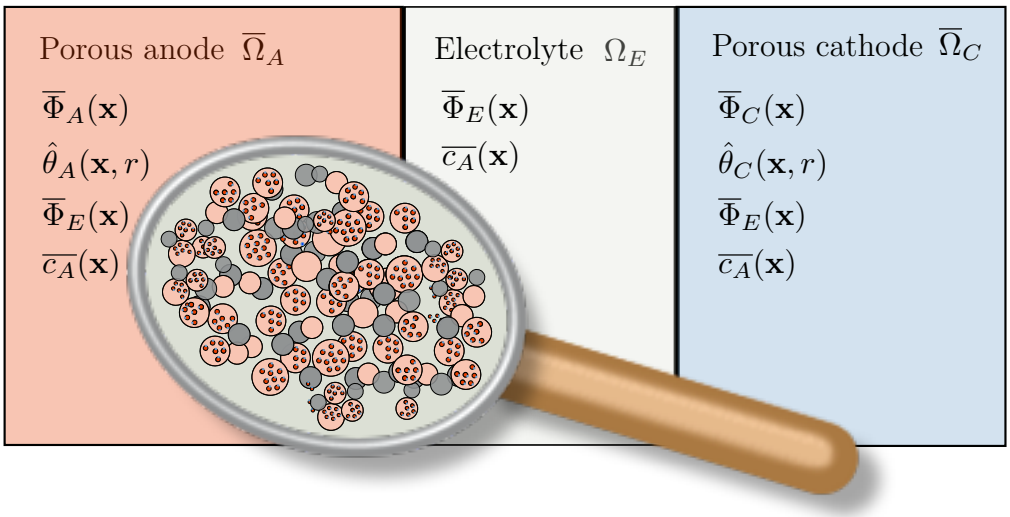

Figure 3.10.: Sketch of a porous cell, consisting of a porous anode $\overline{\Omega}_A$, an electrolyte domain Ω_E, and a porous cathode $\overline{\Omega}_C$.

The porous cathode is described by the same properties, however, with $\overline{\Omega}_C = \Omega_C \times [0, r_C]$ and $\hat{\theta}_C(\mathbf{x}, r)$ as amount of intercalated lithium as well as $\overline{\Phi}_C(\mathbf{x})$ for the averaged potential in the cathode. The electrolyte domain is thus simply described with

- $\mathbf{x} \in \Omega_E$,
- the averaged (electrochemical) potential of charge $\overline{\Phi}_E(\mathbf{x})$
- and the anion concentration $\overline{c_A}(\mathbf{x})$. 3.102. The complete structure of the model is summarized in figure 3.10

The incorporation of the heat equation in terms of averaged quantities is straight forward. However, its explicit derivation is not given here and subject to a further publication.

3.5 Reaction models and boundary conditions

The central concept in electrochemical reaction models is the so called *overpotential*[53]. Consider an electron transfer reaction $\mathrm{C}^+ + \mathrm{e}^- \rightleftharpoons \mathrm{C}$ in equilibrium at some interface Σ_A, *i.e.*

$$\underset{\mathrm{a}}{\overline{\mu}_{C^+}} + \underset{\mathrm{a}}{\overline{\mu}_{e^-}} = \underset{\mathrm{a}}{\overline{\mu}_C}. \tag{3.120}$$

With the definition of electrostatic potential of charge in the electrolyte phase one could write

$$\frac{\overline{\mu}_C - \overline{\mu}_C}{e_0 z_C}\Big|_a = \widetilde{\Phi}\Big|_a - \Phi\Big|_a \tag{3.121}$$

and thus, since $\overline{\mu}_C\big|_a = 0$

$$\underset{\mathrm{a}}{\overline{\mu}}_{C^+} = e_0 \cdot \left(\widetilde{\Phi}_E\big|_a - \Phi\big|_a\right). \tag{3.122}$$

Quite similar one obtains for the electrons

$$\underset{\mathrm{a}}{\overline{\mu}}_{e^-} = -e_0 \cdot \left(\widetilde{\Phi}_A\big|_a - \Phi\big|_a\right) \tag{3.123}$$

and thus

$$\underset{\mathrm{a}}{\overline{\mu}}_{C^+} + \underset{\mathrm{a}}{\overline{\mu}}_{e^-} = e_0 \cdot \left(\widetilde{\Phi}_E\big|_a - \widetilde{\Phi}_A\big|_a\right) \overset{!}{=} \underset{\mathrm{a}}{\overline{\mu}}_C. \tag{3.124}$$

In terms of the averaged quantity, this equation implies in the porous anode

$$e_0 \cdot (\overline{\Phi}_E(\mathbf{x}) - \overline{\Phi}_A(\mathbf{x})) = \overline{\mu}_A(\overline{\theta}(\mathbf{x}, r_A)) \qquad \mathbf{x} \in \Omega_A. \tag{3.125}$$

This remarkable equation is the field theoretical extension of equilibrium condition in a porous electrode. With a simple mixture model of intercalated ions on a lattice (*c.f.* section 2.10.2) one obtains

$$\overline{\theta}(\mathbf{x}, r_A) = \frac{\mathrm{e}^{-\frac{e_0}{k_\mathrm{B}T}\left(\frac{\psi_C^\mathrm{R}}{e_0} - \overline{\Phi}_E(\mathbf{x}) - \overline{\Phi}_A(\mathbf{x})\right)}}{1 + \mathrm{e}^{-\frac{e_0}{k_\mathrm{B}T}\left(\frac{\psi_C^\mathrm{R}}{e_0} - \overline{\Phi}_E(\mathbf{x}) - \overline{\Phi}_A(\mathbf{x})\right)}}. \tag{3.126}$$

This is the porous equilibrium condition in the sense of an equilibrium reaction rate constant.

Auxiliary calculation 3.46:

$$\overline{\mu}_A(\overline{\theta}(\mathbf{x}, r_A)) = \psi_C^\mathrm{R} + k_\mathrm{B}T \ln\left(\frac{\overline{\theta}(\mathbf{x}, r_A)}{1 - \overline{\theta}(\mathbf{x}, r_A)}\right) = \frac{1}{e_0} \cdot (\overline{\Phi}_E(\mathbf{x}) - \overline{\Phi}_A(\mathbf{x}))$$

$$\overline{\theta}(\mathbf{x}, r_A) = (1 - \overline{\theta}(\mathbf{x}, r_A)) \cdot \mathrm{e}^{-\frac{e_0}{k_\mathrm{B}T}\left(\frac{\psi_C^\mathrm{R}}{e_0} - \overline{\Phi}_E(\mathbf{x}) - \overline{\Phi}_A(\mathbf{x})\right)}$$

$$\Rightarrow \quad \overline{\theta}(\mathbf{x}, r_A) = \frac{\mathrm{e}^{-\frac{e_0}{k_\mathrm{B}T}\left(\frac{\psi_C^\mathrm{R}}{e_0} - \overline{\Phi}_E(\mathbf{x}) - \overline{\Phi}_A(\mathbf{x})\right)}}{1 + \mathrm{e}^{-\frac{e_0}{k_\mathrm{B}T}\left(\frac{\psi_C^\mathrm{R}}{e_0} - \overline{\Phi}_E(\mathbf{x}) - \overline{\Phi}_A(\mathbf{x})\right)}}$$

According to the entropy principle for (surface) reactions, a thermodynamic consistent reaction rate for the simple reaction $\mathrm{C}^+ + \mathrm{e}^- \rightleftharpoons \mathrm{C}$ is

$$\underset{\mathrm{s}}{q} = \underset{\mathrm{s}}{\ell} \cdot (\underset{\mathrm{a}}{\overline{\mu}}_{C^+} + \underset{\mathrm{a}}{\overline{\mu}}_{e^-} - \underset{\mathrm{a}}{\overline{\mu}}_C) \tag{3.127}$$

with a positive Onsager coefficient $\underset{\mathrm{s}}{\ell}$. The continuity of the chemical potentials, as well as of electrostatic potential Φ, is a general relationship and holds also in the non-equilibrium situation. One could thus rewrite the reaction rate as

$$\underset{\mathrm{s}}{q} = \underset{\mathrm{s}}{\ell} \cdot \left(e_0 \cdot \left(\widetilde{\Phi}_E\big|_a - \widetilde{\Phi}_A\big|_a\right) - \overline{\mu}_C\big|_a\right) \tag{3.128}$$

and in terms of the averaged quantities

$$\underset{\mathrm{s}}{q} = \underset{\mathrm{s}}{\ell} \cdot \left(e_0 \cdot (\overline{\Phi}_E(\mathbf{x}) - \overline{\Phi}_A(\mathbf{x})) - \overline{\mu}_C(\overline{\theta}(\mathbf{x}, r_A)) \right). \tag{3.129}$$

Note that this equation corresponds to the Tafel equation[136].

Experience has, however, shown that an alternative reaction model is more appropriate to describe chemical reactions close to the equilibrium concentrations.
Assume that only a single reaction occurs and recall the affinity λ of a reaction which conserves the total amount of species (*c.f.* page 2.8.2 *ff.*), *i.e.*

$$\sum_{\alpha=1}^{\mathrm{n}} \nu_\alpha = 0. \tag{3.130}$$

The affinity could be written as

$$\lambda = \sum_{\alpha=1}^{\mathrm{n}} \nu_\alpha \overline{\mu}_\alpha = \sum_{\alpha=1}^{\mathrm{n}} \nu_\alpha \cdot \left(\overline{\mu}_\alpha^{\mathrm{R}} + n^{-1} p + k_{\mathrm{B}} T \ln(c_\alpha) \right) \tag{3.131}$$

$$= \underbrace{\sum_{\alpha=1}^{\mathrm{n}} \nu_\alpha \, \overline{\mu}_\alpha^{\mathrm{R}}}_{=:\ln(K^\ominus)} + \sum_{\alpha=1}^{\mathrm{n}} k_{\mathrm{B}} T \, \nu_\alpha \ln(c_\alpha) \tag{3.132}$$

$$= \ln(K^\ominus) + k_{\mathrm{B}} T \, \ln \left(\prod_{\alpha=1}^{\mathrm{n}} c_\alpha^{\nu_\alpha} \right) \tag{3.133}$$

$$= k_{\mathrm{B}} T \, \ln \left(\underbrace{K^\ominus \cdot \prod_{\alpha=1}^{\mathrm{n}} c_\alpha^{\nu_\alpha}}_{>1} \right) > 0. \tag{3.134}$$

Note that $\overline{\mu}_\alpha^{\mathrm{R}} > 0$, which motivates the transformation. $K^\ominus$ is called equilibrium constant of the chemical reaction. The actual proof of

$$K^\ominus \cdot \prod_{\alpha=1}^{\mathrm{n}} c_\alpha^{\nu_\alpha} > 1, \tag{3.135}$$

which is of course only valid in a neighborhood of the equilibrium conditions, is not given here. However, the assumption is quite common in physical chemistry, since it leads to the mass action law[137].

The entropy production due to a single chemical reaction is hence

$$r_{s,r} = q \cdot \lambda = k_{\mathrm{B}} T \; q \cdot \ln \left(K^\ominus \cdot \prod_{\alpha=1}^{\mathrm{n}} c_\alpha^{\nu_\alpha} \right) \tag{3.136}$$

and one could choose the reaction rate q proportional to the argument of the $\ln()$ term, since

$$K^\ominus \cdot \prod_{\alpha=1}^{\mathrm{n}} c_\alpha^{\nu_\alpha} > 1. \tag{3.137}$$

To ensure the non-negativity of $r_{s,r}$ it is thus sufficient to choose

$$q = \ell \cdot \left(K^{\ominus} \cdot \prod_{\alpha=1}^{\mathrm{n}} c_\alpha^{\nu_\alpha} \right). \tag{3.138}$$

Such an reaction model is called **mass action law**, with a **single** Onsager coefficient per reaction.

One could now[17] rewrite the **chosen** reaction rate in terms of chemical potentials, *i.e.*

$$q = \ell \cdot \left(K^{\ominus} \cdot \prod_{\alpha=1}^{\mathrm{n}} c_\alpha^{\nu_\alpha} \right) \tag{3.139}$$

$$= \ell \cdot \exp\left\{ \frac{1}{k_{\mathrm{B}} T} \cdot \sum_{\alpha=1}^{\mathrm{n}} \nu_\alpha \overline{\mu}_\alpha \right\}. \tag{3.140}$$

The detour via the explicit resolution of the chemical potential was used for clarity reasons. Of course, one could also assume in the very beginning of the reaction model derivation the condition

$$\sum_{\alpha=1}^{\mathrm{n}} \nu_\alpha \overline{\mu}_\alpha > 0, \tag{3.141}$$

in a surrounding of the equilibrium. Note however, that quite far away from equilibrium this condition is **not necessarily** valid. Since the Onsager coefficient ℓ is non-negative it could also be rewritten as

$$\ell = \mathrm{e}^{\alpha_T}. \tag{3.142}$$

Using this approach to model the electrochemical surface reaction $\mathrm{C}^+ + \mathrm{e}^- \rightleftharpoons \mathrm{C}$, the explicit reaction rate

$$\underset{\mathrm{s}}{q} = \mathrm{e}^{\frac{\alpha}{k_{\mathrm{B}} T} \cdot (\underset{\mathrm{a}}{\overline{\mu}_{C^+}} + \underset{\mathrm{a}}{\overline{\mu}_{e^-}} - \underset{\mathrm{a}}{\overline{\mu}_C})} \tag{3.143}$$

is obtained which in terms of the averaged quantities is

$$\underset{\mathrm{s}}{q} = \underset{\mathrm{s}}{\ell} \cdot \mathrm{e}^{\alpha_T \frac{e_0}{k_{\mathrm{B}} T} \cdot (\overline{\Phi}_E(\mathbf{x}) - \overline{\Phi}_A(\mathbf{x})) - \frac{\alpha_T}{k_{\mathrm{B}} T} \overline{\mu}_A(\hat{\theta}(\mathbf{x}, r_A))} \tag{3.144}$$

$$= \mathrm{e}^{\alpha_T \frac{e_0}{k_{\mathrm{B}} T} \cdot (\overline{\Phi}_E(\mathbf{x}) - \overline{\Phi}_A(\mathbf{x}) - \frac{\psi_C^{\mathrm{R}}}{e_0}) - \alpha_T \ln\left(\frac{\hat{\theta}(\mathbf{x}, r_A)}{1 - \hat{\theta}(\mathbf{x}, r_A)} \right)} \tag{3.145}$$

$$= \left(\frac{\hat{\theta}(\mathbf{x}, r_A)}{1 - \hat{\theta}(\mathbf{x}, r_A)} \right)^{\alpha_T} \cdot \mathrm{e}^{\alpha_T \frac{e_0}{k_{\mathrm{B}} T} \cdot (\overline{\Phi}_E(\mathbf{x}) - \overline{\Phi}_A(\mathbf{x}) - \frac{\psi_C^{\mathrm{R}}}{e_0})}. \tag{3.146}$$

The abbreviation

$$i_0 = \mathrm{e}^{\frac{\alpha_T}{k_{\mathrm{B}} T} \psi_C^{\mathrm{R}}} \tag{3.147}$$

is called **exchange current density**[138] and is the equivalent of the equilibrium reaction constant for electrochemical reactions. Note that the transference number α_T is a **phenomenological** constant, *i.e.* an Onsager coefficient, and not an equilibrium property.

[17] Note that due to the assumption $K^{\ominus} \cdot \prod_{\alpha=1}^{\mathrm{n}} c_\alpha^{\nu_\alpha} > 1$ this **not** a vicious circle.

The actual (averaged) source or sink of C^+, e^- and C is (with $\nu_{C^+} = 1$, $\nu_{e^-} = 1$ and $\nu_C = -1$) hence

$$\underset{\mathrm{s}}{r}{}^I_\alpha(\hat{\theta}, \overline{\Phi}_E, \overline{\Phi}_I) = \nu_\alpha \cdot i_0 \left(\frac{\hat{\theta}(\mathbf{x}, r_A)}{1 - \hat{\theta}(\mathbf{x}, r_A)} \right)^{\alpha_T} \cdot \mathrm{e}^{\alpha_T \frac{e_0}{k_\mathrm{B} T} \cdot (\overline{\Phi}_E(\mathbf{x}) - \overline{\Phi}_A(\mathbf{x}))} . \tag{3.148}$$

It couples the averaged balance equations as source term for $(\overline{\Phi}_I, \overline{\Phi}_E)$ **and** as a flux boundary condition for $\hat{\theta}_I$, $I = A, C$. Contributions on the reaction rate due to variations of the cation concentration in the electrolyte phase are implicitly covered in the electrochemical potential $\widetilde{\Phi}_E$. This equation is called **general Butler–Volmer-equation**, as it completely covers variations of the open circuit potential due to the amount of intercalated lithium, in contrast to most classical modeling approaches[55, 97, 106].

I already mentioned above that most porous electrode theory models introduce an additional parameter $U^{\mathrm{fit}}(\theta)$ which is *fitted* to experimental measurements. This error enters **again** in the porous media reaction rate model (*i.e.* the Butler–Volmer-equation) due to the continuity of the surface chemical potential. The above results are therefore to be understood a first step in the direction of a self consistent incorporation of the open circuit potential in porous electrode theory, by providing a thermodynamic basis of the required modeling framework.

3.6 Summary

I have reviewed the whole modeling process for a mathematical description of a lithium ion intercalation battery based on non-equilibrium thermodynamics.

The transport equations for anions, cations and solvent molecules in the electrolyte phase were derived in their most general form and gradually simplified due to reasonable physical assumptions. As a consequence, two branches of model approaches for the electrolyte phase were derived. General Poisson–Nernst–Planck type resolve the actual charge region of an electrode/electrolyte interface and can be used to compute the capacity of an electrochemical interface. The necessity of PNP equations arises essentially when the assumption of a constant charge region looses validity. *Strong* electroneutrality, however, assumes that no charge separation occurs on scales larger than the Debye length, or equivalently, that space charge density $n^\mathrm{F} = 0$, and thus simplifies the whole equation system (in fact, it also decouples the system).

The thermodynamics framework of chapter 2 was then used further used to model a single electrode particle, which obeys a regular solution model. Incorporation of energy contributions from the phase boundary, *i.e.* concentration gradients, to the overall free energy led to Cahn–Hilliard-type (diffusion) equations for intercalated lithium in a single electrode particle. On a two particle example it was shown that bifurcation points in the thermodynamic equilibrium condition arise if the regular solution parameter γ excesses some bound. To model realistic electrodes on the 100μm scale, porous electrode theory was derived with some volume averaging techniques. This method led to homogenized balance equations for the charge density n^F in the electrode and the electrolyte phase (generalized ohmic law) and to homogenized transport equations for anions in the electrolyte and intercalated cations in the electrode phase. The equation system is closed with a thermodynamic consistent reaction rate model, *i.e.* a Butler–Volmer equation for a porous cell.

A

Appendix

A.1 Basics tensor calculus

The following conventions for the typeface of scalars, vectors and matrices are made

- tensor of rank 0 are denoted by small latin letters, *e.g.* a
- tensor of rank 1 are denoted by bold small latin letters, *e.g.* $\mathbf{a}$
- tensor of rank 2 are denoted by bold capital latin letters *e.g.* $\mathbf{A}$ or bold small greek letters (*e.g.* $\boldsymbol{\sigma}$).

Since the application of tensor calculus is restricted to the application of non-relativistic physics, if not stated otherwise, the common space variable is $\mathbf{x} = (x_1, x_2, x_3)^{\mathrm{T}} \in \mathbb{R}^3$ and $\mathbf{e}_1 = (1,0,0)^{\mathrm{T}}$, $\mathbf{e}_2 = (0,1,0)^{\mathrm{T}}$ and $\mathbf{e}_3 = (0,0,1)^{\mathrm{T}}$ denotes the standard or canonical basis, *i.e.* $\mathbf{x} = \sum_{k=1}^{3} x_k \mathbf{e}_k$. Components of vectors and matrices are a_k, $(k = 1,2,3)$ and $a_{j,k}$, $(k,j = 1,2,3)$, respectively.

The operator $\cdot$ denotes the matrix multiplication. For $\mathbf{A} \in \mathbb{R}^{n\times m}$ and $\mathbf{B} \in \mathbb{R}^{n\times k}$ the operation $\cdot : \mathbb{R}^{n\times m} \times \mathbb{R}^{n\times k} \to \mathbb{R}^{k\times m}$ is defined as

$$\mathbf{A} \cdot \mathbf{B} = \left(c_{i,j}\right)_{\substack{i=1,\dots,k \\ j=1,\dots,m}} = \mathbf{C} \tag{A.1}$$

$$c_{i,j} = \sum_{\ell=1}^{n} a_{\ell,i}\, b_{\ell,j}. \tag{A.2}$$

Particularly, for vectors $\mathbf{a}^{\mathrm{T}}$ and $\mathbf{b}$ the scalar product is preserved,

$$\mathbf{a}^{\mathrm{T}} \cdot \mathbf{b} = \sum_{k=1}^{3} a_k b_k = \langle \mathbf{a}, \mathbf{b} \rangle \tag{A.3}$$

The operator $\times$ is the cross product, *i.e.* for $\mathbf{a} \in \mathbb{R}^3$ and $\mathbf{b} \in \mathbb{R}^3$ simply

$$\mathbf{a} \times \mathbf{b} = \begin{pmatrix} a_2 b_3 - a_3 b_2 \\ a_3 b_1 - a_1 b_3 \\ a_1 b_2 - a_2 b_1 \end{pmatrix} = -\mathbf{b} \times \mathbf{a} \tag{A.4}$$

and fulfills the Jacobi identity

$$\mathbf{a} \times (\mathbf{b} \times \mathbf{c}) + \mathbf{c} \times (\mathbf{a} \times \mathbf{b}) + \mathbf{b} \times (\mathbf{c} \times \mathbf{a}) = 0. \tag{A.5}$$

Further, for a matrix $\mathbf{A} \in \mathbb{R}^{3\times 3}$

$$(\mathbf{A}\mathbf{b}) \times (\mathbf{A}\mathbf{c}) = \det(\mathbf{A})\, \mathbf{A}^{-\mathrm{T}} \cdot (\mathbf{b} \times \mathbf{c}). \tag{A.6}$$

With $\otimes : \mathcal{A} \times \mathcal{B} \to \mathcal{A} \otimes \mathcal{B}$ the general tensor product is denoted. For vectors $\mathbf{a} \in \mathbb{R}^3$ and $\mathbf{b} \in \mathbb{R}^3$ it is the dyadic product $\otimes : \mathbb{R}^3 \times \mathbb{R}^3 \to \mathbb{R}^{3\times 3}$

$$\mathbf{a} \otimes \mathbf{b} = \mathbf{a} \cdot \mathbf{b}^{\mathrm{T}} = (a_j b_k)_{j,k} = (b_1\mathbf{a}, b_2\mathbf{a}, b_3\mathbf{a}) = \begin{pmatrix} a_1b_1 & a_1b_2 & a_1b_3 \\ a_2b_1 & a_2b_2 & a_2b_3 \\ a_3b_1 & a_3b_2 & a_3b_3 \end{pmatrix} = (\mathbf{b} \otimes \mathbf{a})^{\mathrm{T}}. \tag{A.7}$$

The left tight operations for a dyadic and a vector are then

$$\mathbf{c} \cdot (\mathbf{a} \otimes \mathbf{b}) = (\mathbf{c} \cdot \mathbf{a})\, \mathbf{b} \tag{A.8}$$

$$(\mathbf{a} \otimes \mathbf{b}) \cdot \mathbf{c} = \mathbf{a}\, (\mathbf{b} \cdot \mathbf{c}). \tag{A.9}$$

The analogy of a scalar product between two tensors is $\bullet : \mathbb{R}^{3\times 3} \times \mathbb{R}^{3\times 3} \to \mathbb{R}$, called tensor scalar product, and

$$\mathbf{A} \bullet \mathbf{B} = \sum_{k=1}^{3} \sum_{j=1}^{3} a_{k,j}\; b_{j,k}. \tag{A.10}$$

In the context of tensor calculus a variety of derivatives occur.

- For a scalar a the linear operator $\nabla : \mathscr{C}^\infty(\mathbb{R}^1) \to \mathscr{C}^\infty(\mathbb{R}^3)$ is called gradient of a and

$$\nabla a = \left(\frac{\partial a}{\partial x_1}, \frac{\partial a}{\partial x_2}, \frac{\partial a}{\partial x_3} \right)^{\mathrm{T}} = \sum_{k=1}^{3} \frac{\partial\, a}{\partial\, x_k} \mathbf{e}_k \tag{A.11}$$

- For a tensor $\mathbf{a}$ of rank 1 the linear operator $\operatorname{div} : \mathbb{R}^3 \to \mathbb{R}$ is called divergence of $\mathbf{a}$ and

$$\operatorname{div} \mathbf{a} = \sum_{k=1}^{3} \frac{\partial a_k}{\partial x_k} = \sum_{k=1}^{3} \langle \partial_{\mathbf{e}_k} \mathbf{a}, \mathbf{e}_k \rangle\,, \tag{A.12}$$

  whereas the operator $\boldsymbol{\nabla} := \otimes\nabla : \mathscr{C}^\infty(\mathbb{R}^3) \to \mathscr{C}^\infty(\mathbb{R}^{3\times 3})$ is

$$(\nabla \otimes \mathbf{a})^{\mathrm{T}} = \boldsymbol{\nabla}\mathbf{a} = \left(\frac{\partial a_j}{\partial x_k} \right)_{j,k} = \begin{pmatrix} \frac{\partial\, a_1}{\partial\, x_1} & \frac{\partial\, a_1}{\partial\, x_2} & \frac{\partial\, a_1}{\partial\, x_3} \\ \frac{\partial\, a_2}{\partial\, x_1} & \frac{\partial\, a_2}{\partial\, x_2} & \frac{\partial\, a_2}{\partial\, x_3} \\ \frac{\partial\, a_3}{\partial\, x_1} & \frac{\partial\, a_3}{\partial\, x_2} & \frac{\partial\, a_3}{\partial\, x_3} \end{pmatrix} = \mathbf{J}_{\mathbf{a}} \tag{A.13}$$

  and called gradient of rank 1 tensor, vector gradient or Jacobian. A bold $\boldsymbol{\nabla}$ will be used to emphasize the tensorial character of the operation.

A frequently used relationship is

$$\begin{pmatrix} \langle \nabla a_1, \mathbf{b} \rangle \\ \langle \nabla a_2, \mathbf{b} \rangle \\ \langle \nabla a_3, \mathbf{b} \rangle \end{pmatrix} = \begin{pmatrix} \sum_{k=1}^{3} \frac{\partial a_1}{\partial x_k} b_k \\ \sum_{k=1}^{3} \frac{\partial a_2}{\partial x_k} b_k \\ \sum_{k=1}^{3} \frac{\partial a_3}{\partial x_k} b_k \end{pmatrix} = \boldsymbol{\nabla} \mathbf{a} \cdot \mathbf{b} \tag{A.14}$$

$$= \langle \mathbf{a}, \nabla \rangle \, \mathbf{b} \tag{A.15}$$

The typeface of equation (A.15) is somehow dangerous, since $\langle \mathbf{a}, \nabla \rangle$ is obviously an operator and thus does not necessarily commute. Nevertheless, this typeface is sometimes useful.

- For a tensor $\mathbf{a}$ of rank 1 (here only $\mathbf{a} \in \mathscr{C}^\infty(\mathbb{R}^3)$ is assumed), the linear operator $\operatorname{curl} : \mathscr{C}^\infty(\mathbb{R}^3) \to \mathscr{C}^\infty(\mathbb{R}^3)$ is called curl and

$$\operatorname{curl} \mathbf{a} := \begin{pmatrix} \frac{\partial a_3}{\partial x_2} - \frac{\partial a_2}{\partial x_3} \\ \frac{\partial a_1}{\partial x_2} - \frac{\partial a_3}{\partial x_1} \\ \frac{\partial a_2}{\partial x_1} - \frac{\partial a_1}{\partial x_2} \end{pmatrix} = \sum_{i,j,k=1}^{3} \epsilon_{i,j,k} \partial_{\mathbf{e}_j} a_k \, \mathbf{e}_i. \tag{A.16}$$

- For a tensor $\mathbf{A}$ of rank 2 the linear operator $\operatorname{Div} : \mathscr{C}^\infty(\mathbb{R}^{3\times 3}) \to \mathscr{C}^\infty(\mathbb{R}^3)$ is called tensor divergence of $\mathbf{A} = (\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3)$ (*i.e.* $\mathbf{a}_k$ are the column vectors of $\mathbf{A}$) and

$$\operatorname{Div} \mathbf{A} := \begin{pmatrix} \sum_{k=1}^{3} \frac{\partial a_{k,1}}{\partial x_k} \\ \sum_{k=1}^{3} \frac{\partial a_{k,2}}{\partial x_k} \\ \sum_{k=1}^{3} \frac{\partial a_{k,2}}{\partial x_k} \end{pmatrix} = \begin{pmatrix} \operatorname{div} \mathbf{a}_1 \\ \operatorname{div} \mathbf{a}_2 \\ \operatorname{div} \mathbf{a}_3 \end{pmatrix} = \left(\sum_{k=1}^{3} \frac{\partial a_{k,j}}{\partial x_k} \right)_j . \tag{A.17}$$

Note that the divergence operates on the **columns's** of $\mathbf{A}$. If $\mathbf{A}$ is a dyadic product, this leads then to generalized product product rule for dyads, *i.e.*

$$\operatorname{Div} (\mathbf{a} \otimes \mathbf{b}) = \begin{pmatrix} \operatorname{div} (b_1 \mathbf{a}) \\ \operatorname{div} (b_2 \mathbf{a}) \\ \operatorname{div} (b_3 \mathbf{a}) \end{pmatrix} = \begin{pmatrix} \langle \nabla b_1, \mathbf{a} \rangle \\ \langle \nabla b_2, \mathbf{a} \rangle \\ \langle \nabla b_3, \mathbf{a} \rangle \end{pmatrix} + (\operatorname{div} \mathbf{a}) \cdot \mathbf{b} \tag{A.18}$$

$$= \boldsymbol{\nabla} \mathbf{b} \cdot \mathbf{a} + (\operatorname{div} \mathbf{a}) \cdot \mathbf{b}. \tag{A.19}$$

Further $\langle \operatorname{Div} \mathbf{A}, \mathbf{b} \rangle = \operatorname{div} (\mathbf{A}^{\mathrm{T}} \cdot \mathbf{b})$ holds for arbitrary vector fields $\mathbf{b}$.

Similar to above, the gradient of a second rank tensor $\nabla \otimes : \mathscr{C}^\infty(\mathbb{R}^{3\times 3}) \to \mathscr{C}^\infty(\mathbb{R}^{3\times 3\times 3})$ is defined as

$$\nabla \otimes \mathbf{A} = \left(\frac{\partial a_{j,k}}{\partial x_\ell} \right)_{k,j,\ell} \tag{A.20}$$

and a tensor of rank 3. If ever used, it will explicitly be called gradient of rank 2 tensor.

To fully exploit the compact typeface of tensor notations, a set of identities is listed, without further proof.

$$\mathbf{c}\cdot(\mathbf{a}\otimes\mathbf{b}) = (\mathbf{c}\cdot\mathbf{a})\,\mathbf{b} \tag{A.21}$$
$$\mathbf{c}\times(\mathbf{a}\otimes\mathbf{b}) = (\mathbf{c}\times\mathbf{a})\otimes\mathbf{b} \tag{A.22}$$
$$(\mathbf{a}\otimes\mathbf{b})\cdot\mathbf{c} = \mathbf{a}\,(\mathbf{b}\cdot\mathbf{c}) \tag{A.23}$$
$$(\mathbf{a}\otimes\mathbf{b})\times\mathbf{c} = \mathbf{a}\otimes(\mathbf{b}\times\mathbf{c}) \tag{A.24}$$
$$\mathbf{a}\cdot(\mathbf{C}\cdot\mathbf{b}) = (\mathbf{a}\otimes\mathbf{b})\bullet\mathbf{C} \tag{A.25}$$
$$\mathrm{Div}\ (\mathbf{a}\otimes\mathbf{b}) = \boldsymbol{\nabla}\mathbf{b}\cdot\mathbf{a} + (\mathrm{div}\,\mathbf{a})\cdot\mathbf{b} \tag{A.26}$$
$$\mathrm{div}\ (\mathbf{B}\cdot\mathbf{a}) = (\mathrm{Div}\,\mathbf{B})\cdot\mathbf{a} + \mathbf{B}\bullet\boldsymbol{\nabla}\mathbf{a} \tag{A.27}$$
$$\mathbf{a}\times(\mathbf{b}\times\mathbf{c}) = \langle\mathbf{a},\mathbf{c}\rangle\,\mathbf{b} - \langle\mathbf{a},\mathbf{b}\rangle\,\mathbf{c} = ((\mathbf{b}\otimes\mathbf{a}) - \langle\mathbf{a},\mathbf{b}\rangle\,\mathbf{Id})\cdot\mathbf{c} \tag{A.28}$$
$$\mathrm{div}\ ((\mathbf{a}\otimes\mathbf{b})\cdot\mathbf{c}) = \mathrm{div}\ (\mathbf{a}(\mathbf{b}\cdot\mathbf{c})) \tag{A.29}$$
$$\mathrm{div}\ ((\mathbf{a}\otimes\mathbf{b})\cdot\mathbf{c}) = (\mathrm{div}\ (\mathbf{a}\otimes\mathbf{b}))\cdot\mathbf{c} + (\mathbf{a}\otimes\mathbf{b})\bullet\boldsymbol{\nabla}\mathbf{c} \tag{A.30}$$
$$\mathrm{div}\ (\mathbf{a}(\mathbf{b}\cdot\mathbf{c})) = \mathbf{a}\cdot\nabla\left(\mathbf{b}\cdot\mathbf{c}^{\mathrm{T}}\right) + (\mathbf{b}\cdot\mathbf{c})\,\mathrm{div}\,\mathbf{a} \tag{A.31}$$
$$\nabla(\mathbf{a}\cdot\mathbf{b}) = \nabla(\langle\mathbf{a},\mathbf{b}\rangle) = \boldsymbol{\nabla}\mathbf{a}\cdot\mathbf{b} + \boldsymbol{\nabla}\mathbf{b}\cdot\mathbf{a} \tag{A.32}$$
$$\mathrm{Div}\,(a\cdot\mathbf{Id}) = \nabla a \tag{A.33}$$
$$\mathrm{tr}(\mathbf{a}\otimes\mathbf{b}) = \langle\mathbf{a},\mathbf{b}\rangle \tag{A.34}$$
$$\mathrm{tr}(\boldsymbol{\nabla}\mathbf{a}) = \mathrm{div}\,\mathbf{a} \tag{A.35}$$
$$\mathrm{curl}\,(\mathbf{b}\times\mathbf{a}) = \mathrm{Div}\ (\mathbf{a}\otimes\mathbf{b} - \mathbf{b}\otimes\mathbf{a}) \tag{A.36}$$
$$= \mathrm{Div}\ (\mathbf{a}\otimes\mathbf{b}) - \boldsymbol{\nabla}\mathbf{a}\cdot\mathbf{b} - (\mathrm{div}\,\mathbf{b})\cdot\mathbf{a} \tag{A.37}$$
$$= \boldsymbol{\nabla}\mathbf{b}\cdot\mathbf{a} + (\mathrm{div}\,\mathbf{a})\cdot\mathbf{b} - \boldsymbol{\nabla}\mathbf{a}\cdot\mathbf{b} - (\mathrm{div}\,\mathbf{b})\cdot\mathbf{a} \tag{A.38}$$
$$(\mathrm{curl}\,\mathbf{a})\times\mathbf{b} = \mathrm{Div}\,(\mathbf{b}\otimes\mathbf{a} - \langle\mathbf{a},\mathbf{b}\rangle\cdot\mathbf{Id}) - \mathbf{a}\cdot\mathrm{div}\,\mathbf{b} + \boldsymbol{\nabla}\mathbf{b}\cdot\mathbf{a} \tag{A.39}$$
$$= \mathrm{Div}\,(\mathbf{b}\otimes\mathbf{a} - \frac{1}{2}\langle\mathbf{a},\mathbf{b}\rangle\cdot\mathbf{Id}) - \mathbf{a}\cdot\mathrm{div}\,\mathbf{b} + \frac{1}{2}(\boldsymbol{\nabla}\mathbf{b}\cdot\mathbf{a} - \boldsymbol{\nabla}\mathbf{a}\cdot\mathbf{b}) \tag{A.40}$$
$$\mathrm{div}\,(\mathbf{a}\times\mathbf{b}) = (\mathrm{curl}\,\mathbf{a})\cdot\mathbf{b}^{\mathrm{T}} - (\mathrm{curl}\,\mathbf{b})\cdot\mathbf{a}^{\mathrm{T}} \tag{A.41}$$

Theorem 10 (Jacobi's formula of matrix calculus)**.**

For a differentiable second rank tensor field $\mathbf{A} = \mathbf{A}(s)$ with $\mathbf{A}(s) \neq 0\ \forall t$ the following relationship holds,

$$\frac{\mathrm{d}\ \det(\mathbf{A}(s))}{\mathrm{d}t} = \det(\mathbf{A})\,\mathrm{tr}\left(\frac{\mathrm{d}\,\mathbf{A}}{\mathrm{d}s}\,\mathbf{A}^{-1}\right). \tag{A.42}$$

Proof. See [139, p.18] □

Lemma 4 (Derivative of a parametrized, inverse Matrix)**.**

For a parametrized Matrix $\mathbf{A} = \mathbf{A}(s) \in \mathscr{C}^{\infty}(\mathbb{R}^{n\times n})$ with $\det(\mathbf{A}) \neq 0\ \forall s \in I$

$$\frac{\mathrm{d}\,\mathbf{A}^{-1}}{\mathrm{d}s} = -\mathbf{A}^{-1}\frac{\mathrm{d}\,\mathbf{A}}{\mathrm{d}s}\mathbf{A}^{-1} \tag{A.43}$$

Lemma 5 (Chain rule for vector gradients)**.**

Let $\mathbf{a} :\in \mathscr{C}^{\infty}(\mathbb{R}^3)$, $\mathbf{x} \in \Omega \subset \mathbb{R}^3$ and $(\boldsymbol{\xi}, t) \mapsto (\boldsymbol{\chi}(\boldsymbol{\xi}, t), t)$ be a diffeomorphism. Then

$$\boldsymbol{\nabla}_{\boldsymbol{\xi}}\mathbf{a}(\boldsymbol{\chi}(\boldsymbol{\xi}, t)) = \boldsymbol{\nabla}_{\mathbf{x}}\mathbf{a}(\mathbf{x})\cdot\boldsymbol{\nabla}_{\boldsymbol{\xi}}\boldsymbol{\chi}. \tag{A.44}$$

Lemma 6 (Chain rule for parametrized scalar and vector fields)**.**

Let $\mathbf{a} \in \mathscr{C}^\infty(\mathbb{R}^3)$, $\mathbf{x} \in \Omega \subset \mathbb{R}^3$ and $\mathbf{b} \in \mathscr{C}^\infty(\mathbb{R}^3)$, $\mathbf{x} \in \Omega \subset \mathbb{R}^3$. Consider a diffeomorphism $(\boldsymbol{\xi}, t) \mapsto (\boldsymbol{\chi}(\boldsymbol{\xi}, t), t)$ with

$$\frac{\partial \boldsymbol{\chi}(\boldsymbol{\xi}, t)}{\partial t} = \mathbf{v}'(\boldsymbol{\xi}, t). \tag{A.45}$$

Then

$$\frac{\mathrm{d}\, a(\boldsymbol{\chi}(\boldsymbol{\xi}, t))}{\mathrm{d}t} = \langle \nabla a, \mathbf{v}' \rangle \tag{A.46}$$

$$\frac{\mathrm{d}\, \mathbf{b}(\boldsymbol{\chi}(\boldsymbol{\xi}, t))}{\mathrm{d}t} = \boldsymbol{\nabla} \mathbf{b} \cdot \mathbf{v}' \tag{A.47}$$

A.2 Differential geometry basics

Definition 13 (Coordinate free divergence)**.**

The divergence of an arbitrary vector field $\mathbf{a}$ at a fixed point $\mathbf{x}_0 \in \Omega$ is defined as

$$\operatorname{div} \mathbf{a}(\mathbf{x}_0) = \lim_{\mathrm{vol}\{\Omega\} \to 0} \frac{1}{\mathrm{vol}\{\Omega\}} \oint_{\partial\Omega} \mathbf{a}^{\mathrm{T}}(\mathbf{x}) \cdot d\mathbf{A}(\mathbf{x}). \tag{A.48}$$

Since this definition is independent of a specific parametrization of the surface $\partial\Omega$, it is called *coordinate free*. For an identity $\mathbf{a}(\mathbf{x}) = \mathbf{b}(\boldsymbol{\xi})$ the coordinate free divergence states

$$\operatorname{div}_{\mathbf{x}} \mathbf{a}(\mathbf{x}) = \operatorname{div}_{\boldsymbol{\xi}} \mathbf{b}(\boldsymbol{\xi}). \tag{A.49}$$

Definition 14 (Coordinate free Curl)**.**

The curl of an arbitrary vector field $\mathbf{a}$ at a fixed point $\mathbf{x}_0 \in \Sigma$ is defined as

$$\langle \operatorname{curl} \mathbf{a}(\mathbf{x}_0), \mathbf{n}_\Sigma(\mathbf{x}_0) \rangle = \lim_{\mathrm{area}\{\Sigma\} \to 0} \frac{1}{\mathrm{area}\{\Sigma\}} \oint_{\partial\Sigma} \mathbf{a}^{\mathrm{T}}(\mathbf{x}) \cdot d\mathbf{s}(\mathbf{x}), \tag{A.50}$$

where $\mathbf{n}_\Sigma(\mathbf{x}_0)$ is the normal vector of the surface in $\mathbf{x}_0$. Since this definition is independent of a specific parametrization of the surface $\partial\Omega$, it is called *coordinate free*. For an identity $\mathbf{a}(\mathbf{x}) = \mathbf{b}(\boldsymbol{\xi})$ the coordinate free divergence states

$$\operatorname{curl}_{\mathbf{x}} \mathbf{a}(\mathbf{x}) = \operatorname{curl}_{\boldsymbol{\xi}} \mathbf{b}(\boldsymbol{\xi}). \tag{A.51}$$

Theorem 11 (Divergence theorem for rank 1 and 2 tensors)**.**

Let Ω be a bounded domain in $\mathbb{R}^3$ and $\partial\Omega$ be its regular surface. Further, let $\mathbf{a} \in \mathscr{C}^\infty(\mathbb{R}^{3\times 1})$ and $\mathbf{B} \in \mathscr{C}^\infty(\mathbb{R}^{3\times 3})$, then

$$\int_\Omega \operatorname{div} \mathbf{a}\, dV = \int_{\partial\Omega} \mathbf{a}^{\mathrm{T}} \cdot d\mathbf{A} \tag{A.52}$$

$$\int_\Omega \operatorname{Div} \mathbf{B}\, dV = \int_{\partial\Omega} \mathbf{B}^{\mathrm{T}} \cdot d\mathbf{A}. \tag{A.53}$$

Theorem 12 (Kelvin-Stokes theorem)**.**

Let $\Sigma \in \mathbb{R}^3$ be a regular surface, bounded by the curve $\partial\Sigma \in \mathbb{R}^3$. Further, let $\mathbf{f}$ be a

sufficient smooth vector field, then

$$\int_{\Sigma} (\operatorname{curl} \mathbf{f})^{\mathrm{T}} \cdot d\mathbf{A} = \oint_{\partial\Sigma} \mathbf{f}^{\mathrm{T}} \cdot d\mathbf{s} \tag{A.54}$$

Differential geometry of and vector calculus on Surfaces

Corollary 11 (Tangent space of regular surfaces)**.**

Let Σ be a regular surface and $\mathbf{p}(u,v)$, $(u,v) \in S = [0,1]^2$ a (local) parametrization with $\mathbf{p}(S) = \Sigma$. The **tangent space** of Σ in a *fixed* position $\mathbf{x}_0 = \mathbf{p}(u_0, v_0)$ is given by

$$T_{\mathbf{x}_0}(\Sigma) := \mathbf{J}_{\mathbf{p}}(u_0, v_0)(\mathbb{R}^2) = \operatorname{span}\left\{ \left.\frac{\partial \mathbf{p}}{\partial u}\right|_{(u_0,v_0)}, \left.\frac{\partial \mathbf{p}}{\partial v}\right|_{(u_0,v_0)} \right\}. \tag{A.55}$$

The set of all tangent spaces

$$T(\Sigma) := \{(\mathbf{x}, \boldsymbol{\tau}) | \mathbf{x} \in \Sigma, \boldsymbol{\tau} \in T_{\mathbf{x}}(\Sigma)\} \tag{A.56}$$

is called **tangent bundle**. Abbreviating

$$\boldsymbol{\tau}_1(\mathbf{x})\big|_{\mathbf{x}=p(u,v)} = \frac{\partial \mathbf{p}}{\partial u} \tag{A.57}$$

$$\boldsymbol{\tau}_2(\mathbf{x})\big|_{\mathbf{x}=p(u,v)} = \frac{\partial \mathbf{p}}{\partial v}, \tag{A.58}$$

$\boldsymbol{\tau}_1(\mathbf{x})$ and $\boldsymbol{\tau}_2(\mathbf{x})$ form a basis of $T_{\mathbf{x}}(\Sigma)$ and vector fields $\boldsymbol{\tau} \in T_{\mathbf{x}}(\Sigma)$ are called **tangent fields**. A unit normal vector of Σ is deduced from

$$\frac{\boldsymbol{\tau}_1 \times \boldsymbol{\tau}_2}{||\boldsymbol{\tau}_1 \times \boldsymbol{\tau}_2||} =: \mathbf{n} \tag{A.59}$$

and the space

$$N_{\mathbf{x}}(\Sigma) := (T_{\mathbf{x}}(\Sigma))^{\perp} = \{\mathbf{n} \in \mathbb{R}^3 | \mathbf{n} \perp \boldsymbol{\tau} \text{ for all } \boldsymbol{\tau} \in T_{\mathbf{x}}(\Sigma)\} \tag{A.60}$$

is called **normal space** of $\mathbf{x}$ on Σ. Elements $\boldsymbol{\nu}$ of $N_{\mathbf{x}}(\Sigma)$ are called normal fields and

$$N(\Sigma) = \{(\mathbf{x}, \boldsymbol{\nu}) | \mathbf{x} \in \Sigma, \boldsymbol{\nu} \in N_{\mathbf{x}}(\Sigma)\} \tag{A.61}$$

is called **normal bundle** of Σ. The dual space of $T_{\mathbf{x}}(\Sigma)$ is called **cotangent space** $T^*_{\mathbf{x}}(\Sigma)$.

Remark 11 (Tangential and normal decomposition)*.*

Every vector field $\mathbf{b}(\mathbf{x})$, $\mathbf{x} \in \Sigma$ may be decomposed according to

$$\mathbf{b} = b_{\mathbf{n}}(\mathbf{x})\, \mathbf{n} + \underset{\mathrm{s}}{\mathbf{b}}(\mathbf{x}) \tag{A.62}$$

where $\underset{\mathrm{s}}{\mathbf{b}} \in T_{\mathbf{x}}(\Sigma)$ and $b_{\mathbf{n}}\, \mathbf{n} \in N_{\mathbf{x}}(\Sigma)$. The field $b_{\mathbf{n}} \in \mathbb{R}$ is called normal component of $\mathbf{b}$ and $\underset{\mathrm{s}}{\mathbf{b}} \in \mathbb{R}^3$ is called tangential component of $\mathbf{b}$.
For a tangential field $\underset{\mathrm{s}}{\mathbf{a}} \in T_{\mathbf{x}}(\Sigma)$ clearly

$$\left\langle \underset{\mathrm{s}}{\mathbf{a}}, \mathbf{b} \right\rangle = \left\langle \underset{\mathrm{s}}{\mathbf{a}}, \underset{\mathrm{s}}{\mathbf{b}} \right\rangle. \tag{A.63}$$

Definition 15 (Differentiability on surfaces)**.**

Let Σ be an embedded surface in $\mathbb{R}^3$ with an open subset $\Sigma_U \subset \Sigma$, *i.e.* a neighborhood on the surface, where for all $\mathbf{x} \in \Sigma_U$ exists a neighborhood $U \in \mathbb{R}^3$ such that $U \cup \Sigma \subset \Sigma_U$. Then a function $a : \Sigma \to \mathbb{R}$ (or a vector field $\mathbf{b} : \Sigma \to \mathbb{R}^3$) is called continuously differentiable on the surface Σ, **if** for $\mathbf{x} \in \Sigma_U$ and $\boldsymbol{\tau} \in T_{\mathbf{x}}(\Sigma)$ the directional derivative

$$\mathrm{D}_{\mathbf{x}} a(\boldsymbol{\tau}) =: \partial_{\boldsymbol{\tau}} a(\mathbf{x}) = \lim_{\epsilon \to 0} \frac{a(\mathbf{x} + \epsilon \boldsymbol{\tau}) - a(\mathbf{x})}{\epsilon} \tag{A.64}$$

exists, and $\mathrm{D}_{\mathbf{x}} a : T_{\mathbf{x}}(\Sigma) \to \mathbb{R}$ is a linear operator. The surface differentiability of vector fields on the surface is (equivalently) defined column wise.

Remark 12 (Orthogonal basis of $T_{\mathbf{x}}(\Sigma)$).

In general $\boldsymbol{\tau}_1$ and $\boldsymbol{\tau}_2$ are **not** orthogonal. However, one could clearly deduce the orthonormal basis

$$\mathbf{t}_1 = \boldsymbol{\tau}_1 \tag{A.65}$$

$$\mathbf{t}_2 = \boldsymbol{\tau}_2 - \frac{\langle \boldsymbol{\tau}_1, \boldsymbol{\tau}_2 \rangle}{||\boldsymbol{\tau}_1||} \cdot \boldsymbol{\tau}_1. \tag{A.66}$$

Since the directional derivative is a linear operator on $T_{\mathbf{x}}(\Sigma)$ one obtains for a scalar field $a(\mathbf{x})$, $\mathbf{x} \in \Sigma$

$$\mathrm{D}_{\mathbf{x}} a(\boldsymbol{\tau}_1) = \mathrm{D}_{\mathbf{x}} a(\mathbf{t}_1) \tag{A.67}$$

$$\mathrm{D}_{\mathbf{x}} a(\boldsymbol{\tau}_2) = \mathrm{D}_{\mathbf{x}} a(\mathbf{t}_2) + \frac{\langle \boldsymbol{\tau}_1, \boldsymbol{\tau}_2 \rangle}{||\boldsymbol{\tau}_1||} \mathrm{D}_{\mathbf{x}} a(\mathbf{t}_1). \tag{A.68}$$

The tupel $(\mathbf{t}_1, \mathbf{t}_2, \mathbf{n})$ is then an orthonormal basis of $(T_{\mathbf{x}}(\Sigma) \times (T_{\mathbf{x}}(\Sigma))^{\perp}) = \mathbb{R}^3$.

Definition 16 (Surface differential operators)**.**

Let $\Sigma \in \mathbb{R}^3$ be a (regular) surface and $a : \Sigma \to \mathbb{R}$ be a scalar field (and $\mathbf{b} : \Sigma \to \mathbb{R}^3$ be vector field) defined on Σ. For arbitrary $\boldsymbol{\gamma} \in \mathscr{C}^{\infty}(\mathbb{R}^1)$ with $\boldsymbol{\gamma}(t) = \mathbf{x}$, $t \in I \subset \mathbb{R}$, the chain rules holds (for all curves). Since only the products $(\nabla a)^{\mathrm{T}} \cdot \dot{\boldsymbol{\gamma}}$ and $(\boldsymbol{\nabla} \mathbf{b}) \cdot \dot{\boldsymbol{\gamma}}$ appear, the typeface

$$\underset{\mathrm{s}}{\nabla}\, a(\mathbf{x}) \tag{A.69}$$

$$\underset{\mathrm{s}}{\boldsymbol{\nabla}}\, \mathbf{b}(\mathbf{x}) \tag{A.70}$$

will be used to emphasize that $\underset{\mathrm{s}}{\nabla}\, a(\mathbf{x})$ and $\underset{\mathrm{s}}{\boldsymbol{\nabla}}\, \mathbf{b}(\mathbf{x})$ are indeed a surface properties. However, $\underset{\mathrm{s}}{\nabla}\, a(\mathbf{x}) \in \mathbb{R} \otimes T_{\mathbf{x}}\Sigma$ while $(\nabla f)^{\mathrm{T}} \cdot \dot{\boldsymbol{\gamma}} \in \Sigma$ (and similar for $\mathbf{b}$).

Corollary 12 (Surface differential operators of volumetric fields)**.**

Let $a(\mathbf{x})$ and $\mathbf{b}(\mathbf{x})$ be scalar and vector fields with domain $\mathbf{x} \in \Omega$ which are smooth up to some surface $\Sigma \subset \Omega$. The surface differential operators obey then the following relationships

- **Surface gradient**

$$\underset{\mathrm{s}}{\nabla}\, a(\mathbf{x}) = \nabla a(\mathbf{x}) - \langle \nabla a, \mathbf{n} \rangle\, \mathbf{n} \tag{A.71}$$

- **Surface vector gradient (surface jacobian)**

$$\underset{\mathrm{s}}{\boldsymbol{\nabla}}\,\mathbf{b}(\mathbf{x}) = \boldsymbol{\nabla}\mathbf{b}(\mathbf{x}) - (\boldsymbol{\nabla}\mathbf{b}(\mathbf{x})\cdot\mathbf{n})\otimes\mathbf{n} \tag{A.72}$$

- **Surface divergence**

$$\underset{\mathrm{s}}{\operatorname{div}}\,\mathbf{b} = \operatorname{tr}\Big(\underset{\mathrm{s}}{\boldsymbol{\nabla}}\,\mathbf{b}\Big) = \operatorname{tr}(\boldsymbol{\nabla}\mathbf{b}) - \operatorname{tr}((\boldsymbol{\nabla}\mathbf{b}(\mathbf{x})\cdot\mathbf{n})\otimes\mathbf{n}) \tag{A.73}$$

$$= \operatorname{div}\mathbf{b} - \langle\boldsymbol{\nabla}\mathbf{b}(\mathbf{x})\cdot\mathbf{n},\mathbf{n}\rangle \tag{A.74}$$

$$= \operatorname{div}\mathbf{b} - \mathbf{n}^{\mathrm{T}}\cdot(\boldsymbol{\nabla}\mathbf{b})^{\mathrm{T}}\cdot\mathbf{n} \tag{A.75}$$

- **Surface tensor divergence**
  For $\mathbf{C} = (\mathbf{c}_1, \mathbf{c}_2, \mathbf{c}_3)$

$$\underset{\mathrm{s}}{\operatorname{Div}}\,\mathbf{C} = \operatorname{Div}\mathbf{C} - \Big(\mathbf{n}^{\mathrm{T}}\cdot(\boldsymbol{\nabla}\mathbf{c}_k)^{\mathrm{T}}\cdot\mathbf{n}\Big)_k \tag{A.76}$$

- **Surface curl**
  The surface curl is a somehow non-intuitive formulation[140] as it operates on scalar and vector fields. However, it fulfills the properties one expects from a surface curl (*i.e.* a surface Helmholtz theorem, a surface).

$$\underset{\mathrm{s}}{\operatorname{curl}}\,a = \mathbf{n}\times\underset{\mathrm{s}}{\nabla}\,a \tag{A.77}$$

$$\underset{\mathrm{s}}{\operatorname{Curl}}\,\mathbf{b} = \langle\mathbf{n},\operatorname{curl}\mathbf{b}\rangle \tag{A.78}$$

Clearly, the surface gradients are tangential fields, *i.e.* they obey

$$\Big\langle\underset{\mathrm{s}}{\nabla}\,a,\mathbf{n}\Big\rangle = 0 \tag{A.79}$$

$$\Big(\underset{\mathrm{s}}{\boldsymbol{\nabla}}\,\mathbf{b}\Big)\cdot\mathbf{n} = \mathbf{0}. \tag{A.80}$$

Definition 17 (Mean curvature)**.**

Let $\mathbf{n}\in N_{\mathbf{x}}(\Sigma)$ be the normal field of Σ and $N(\Sigma)$ the corresponding normal bundle. The property

$$\kappa =: -\underset{\mathrm{s}}{\operatorname{div}}\,\mathbf{n} \tag{A.81}$$

is called total or **mean curvature** of Σ.[1]

Remark 13 (Useful relationships of surface differential operators).

[1] While in continuum mechanics the definition $\kappa =: -\underset{\mathrm{s}}{\operatorname{div}}\,\mathbf{n}$ is used, classical differential geometry defines the mean curvature as $\kappa =: -\frac{1}{2}\underset{\mathrm{s}}{\operatorname{div}}\,\mathbf{n}$.

$$\underset{\mathrm{s}}{\mathrm{Curl}}\ \mathbf{n} = 0 \tag{A.82}$$

$$\underset{\mathrm{s}}{\mathrm{div}}\ \mathbf{b} = (\underset{\mathrm{s}}{\mathrm{div}}\ \mathbf{n})b_{\mathbf{n}} + \underset{\mathrm{s}}{\mathrm{div}}\ \underset{\mathrm{s}}{\mathbf{b}} = -\kappa b_{\mathbf{n}} + \underset{\mathrm{s}}{\mathrm{div}}\ \underset{\mathrm{s}}{\mathbf{b}} \tag{A.83}$$

$$\underset{\mathrm{s}}{\mathrm{Curl}}\ \mathbf{b} = \underset{\mathrm{s}}{\mathrm{Curl}}\ \underset{\mathrm{s}}{\mathbf{b}} \tag{A.84}$$

$$\underset{\mathrm{s}}{\mathrm{Curl}}\,(\mathbf{n} \times \mathbf{b}) = \underset{\mathrm{s}}{\mathrm{div}}\ \underset{\mathrm{s}}{\mathbf{b}} \tag{A.85}$$

$$\underset{\mathrm{s}}{\mathrm{div}}\,(\mathbf{n} \times \mathbf{b}) = -\underset{\mathrm{s}}{\mathrm{Curl}}\ \underset{\mathrm{s}}{\mathbf{b}} \tag{A.86}$$

Theorem 13 (Surface Gaussian theorem)**.**

Let $\mathbf{a}$ be a sufficient smooth vector field defined in Ω, and let Σ be a surface in Ω. Further, let Σ be bounded by a curve $\partial\Sigma$. With the above definitions and relations of surface gradients and the surface divergence

$$\int_{\Sigma} \underset{\mathrm{s}}{\mathrm{div}}\ \mathbf{a}\, dA = \int_{\Sigma} \left(\underset{\mathrm{s}}{\mathrm{div}}\ \underset{\mathrm{s}}{\mathbf{a}} + a_{\mathbf{n}}\kappa\right)\, dA = \oint_{\partial\Sigma} \mathbf{a}^{\mathrm{T}} \cdot\, d\mathbf{s}. \tag{A.87}$$

Note, for tangential surface fields $\underset{\mathrm{s}}{\mathbf{a}}$ the surface Gaussian theorem reduces to

$$\int_{\Sigma} \underset{\mathrm{s}}{\mathrm{div}}\ \underset{\mathrm{s}}{\mathbf{a}}\, dA = \oint_{\partial\Sigma} \underset{\mathrm{s}}{\mathbf{a}}^{\mathrm{T}} \cdot\, d\mathbf{s}. \tag{A.88}$$

List of Symbols

Domains

Ω	Overall (Eulerian) domain $\subset \mathbb{R}^3$	54
$(\mathbf{x}, \mathbf{v})$	Standard coordinate system with the barycentric velocity $\mathbf{v}$	56
$(\mathbf{y}, \overline{\mathbf{v}})$	Coordinate system with respect to the mean particle velocity	58
$(\hat{\mathbf{v}}, \boldsymbol{\xi})$	Coordinate system with respect to the nþspecies or a lattice	122

General notation

a	Arb. scalar field $a(\mathbf{x}, t), b(\mathbf{x}, t), c(\mathbf{x}, t)$ (tensor of rank 0)	161
$\underset{\mathrm{s}}{a}$	Arb. surface scalar field on a singular surface	21
$\mathbf{a}$	Arb. vector field $\mathbf{a}(\mathbf{x}, t), \mathbf{b}(\mathbf{x}, t), \mathbf{c}(\mathbf{x}, t)$ (tensor of rank 1)	161
$\mathbf{A}$	Arb. matrix field $\mathbf{A}(\mathbf{x}, t), \mathbf{B}(\mathbf{x}, t)$, or $\boldsymbol{\sigma}$ (tensor of rank 2)	161
$\underline{a}$	Arb. vector of vectors, *i.e.* $\underline{a} = (\mathbf{a}_1, \ldots, \mathbf{a}_N)^T$	93
$\underline{\underline{\mathbf{A}}}$	Arb. matrix of matrices, *i.e.* $(\underline{\underline{\mathbf{A}}})_{i,j} = \mathbf{A}_{i,j} \in \mathbb{R}^{3\times 3}$	108

Constants

n	Number of distinguishable species	54
n_r	Number of chemical reactions	59
m_α	Molecular mass of species k	55
z_α	Charge number of species k	55
e_0	Elementary charge, $e_0 = 1.602176 \cdot 10^{-19}$ C	55
k_B	Boltzmann constant, $k_\mathrm{B} = 1.3806488 \cdot 10^{-23}\ \mathrm{J} \cdot \mathrm{K}^{-1}$	119

Volume variables

$\rho_\alpha(\mathbf{x}, t)$	Mass density of species α	55
$\rho(\mathbf{x}, t)$	Mass density ($\rho = \sum_{\alpha=1}^{\mathrm{n}} \rho_\alpha$)	55
$w_\alpha(\mathbf{x}, t)$	Mass fraction ($w_\alpha = \rho_\alpha \cdot \rho^{-1}$)	55
$n_\alpha(\mathbf{x}, t)$	Number density or concentration of species α ($n = m_\alpha^{-1} \cdot \rho_\alpha$)	55
$n(\mathbf{x}, t)$	Number density or amount of species $n = \sum_{\alpha=1}^{\mathrm{n}} n_\alpha$	55
$c_\alpha(\mathbf{x}, t)$	Mole fraction or molar concentration ($c_k = n_\alpha \cdot n^{-1}$)	55
$n_\alpha^{\mathrm{F}}(\mathbf{x}, t)$	Free charge density of species α	55
$n^{\mathrm{F}}(\mathbf{x}, t)$	Free charge density ($n^{\mathrm{F}} = e_0 \sum_{\alpha=1}^{\mathrm{n}} z_\alpha n_\alpha$)	55
n_ℓ	Number density of lattice sites per volume	121
$\theta_\alpha(\mathbf{x}, t)$	Coverage or concentration on a lattice species α ($\theta_\alpha = n_\alpha \cdot n_\ell$)	121
$r_\alpha(\mathbf{x}, t)$	Net mass production of species α	56
$\nu_{k,j}$	Stochiometric coefficient of reaction j and species k	59
$\mathbf{j}_\alpha(\mathbf{x}, t)$	Mass flux of species α	55
$\mathbf{j}^{\mathrm{F}}(\mathbf{x}, t)$	Mass governed electric current ($\mathbf{j}^{\mathrm{F}} = e_0 \sum_{\alpha=1}^{\mathrm{n}} z_\alpha\, m_\alpha^{-1} \mathbf{j}_\alpha$)	55

Thermodynamic properties

ρu	Internal energy density	78
ρs	Entropy density	81
$\rho\psi$	Helmholtz free energy density	99
g	Gibbs free energy density	102
p	Pressure	75
$\boldsymbol{\pi}$	Viscous stress tensor, $\boldsymbol{\sigma} = p\mathbf{Id} + \boldsymbol{\pi}$	75
T	Temperature	83
μ_α	Chemical potential of species α per mass	83
$\overline{\mu}_\alpha$	Chemical potential of species α per particle	107
$\mathbf{j}_u$	Total energy flux	78
$\mathbf{j}_s$	Entropy flux	82
ϑ	Heat	100
$\mathbf{j}_\vartheta$	Heat flux	100
$\mathfrak{s}, \mathfrak{g}, \mathfrak{f}$	Material functions of ρs, g, $\rho\psi$	102

Electrodynamic properties

$\mathbf{E}$	Electric field $\left[\frac{\mathrm{V}}{\mathrm{m}}\right]$	62
$\mathbf{D}$	Electric flux density $\left[\frac{\mathrm{C}}{\mathrm{m}^2}\right]$	62
$\mathbf{B}$	Magnetic flux density $[\mathrm{T}]$	62
$\mathbf{H}$	Magnetic field $\left[\frac{\mathrm{A}}{\mathrm{m}}\right]$	62
$\mathbf{P}$	Polarization vector	64
n^{B}	Bound charge	64
$\mathbf{j}^{\mathrm{B}}$	Polarization or bound charge current	65
$\mathbf{M}$	Magnetization vector	65
$\mathbf{j}^{\mathrm{M}}$	Magnetization current	65

List of Figures

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Hiermit versichere ich, Manuel Landstorfer, dass ich die hier vorliegende, zur Promotion eingereichte Arbeit mit dem Titel *„Mathematical Modeling of Batteries based on Balance Equations and Coupled Thermo-Electrodynamics“* selbstständig verfasst, nur die angegebenen Quellen und Hilfsmittel benutzt, und wörtlich oder inhaltlich übernommene Stellen als solche gekennzeichnet habe. Ich versichere an Eides statt, dass diese Angaben wahr sind und dass ich nichts verschwiegen habe. Ich erkläre außerdem, dass die von mir vorgelegte Dissertation bisher nicht im In- oder Ausland in dieser oder ähnlicher Form in einem anderen Promotionsverfahren vorgelegt wurde. Ich versichere ferner die Richtigkeit der im Lebenslauf gemachten Angaben.

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