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electrochemistry**

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Abstract

In this work, the balance equations of non-equilibrium thermodynamics are coupled to Galilean limit systems of the Maxwell equations, i.e. either to (i) the quasi-electrostatic limit or (ii) the quasi-magnetostatic limit. We explicitly consider a volume Ω which is divided into Ω^+ and Ω^- by a possibly moving singular surface S , where a charged reacting mixture of a viscous medium can be present on each geometrical entity (Ω^+, S, Ω^-) . By the restriction to Galilean limits of the Maxwell equations, we achieve that only subsystems of equations for matter and electric field are coupled that share identical transformation properties with respect to observer transformations. Moreover, the application of an entropy principle becomes more straightforward and finally it helps to estimate the limitations of the more general approach based the full set of Maxwell equations. Constitutive relations are provided based on an entropy principle and particular care is taken for the analysis of the stress tensor and the momentum balance in the general case of non-constant scalar susceptibility. Finally, we summarize the application of the derived model framework to an electrochemical system with surface reactions.

1 Introduction

Reliable simulation of electrochemical systems on the device level requires thermodynamic consistent continuum models. Standard models like the Poisson–Nernst–Planck system suffer from well known limitations, cf. e.g., [3, 16], of which the most obvious deficiency is the missing of volume exclusion effects. Several similar remedies for this problem have been proposed, see e.g., [4, 11, 8] and the literature cited therein. More recent approaches that also take dielectric effects of the solvent into account are e.g. [10] and [13]. The latter one builds on a bulk-surface electro-thermodynamic modeling framework summarized in [9] which unifies classical non-equilibrium thermodynamics containing electromagnetic fields as in [7, 15] and its extensions to surfaces [1, 2]. As an alternative modelling framework, [20] recently developed a multiscale electro-thermodynamics approach within the GENERIC formalism. Although not less complex and technical compared to [9], this approach is so far limited to closed bulk systems.

Applying the abstract framework of [9] to electrochemical problems, typically first requires strong simplifications of the model, thereby favouring the impression that the framework appears too general and not precisely tailored to the considered class of problems. Moreover, the readers of [9] might get confused by some decisions taken there for mainly pragmatic reasons but leading to a discussion of stability conditions that are related to the choice of independent variables and that are necessary in addition to the employed entropy principle. Finally, the way how the electromagnetic sub-system and the classical material mixture part are coupled in [9] might not appear fully satisfactory because of the different transformation properties of these sub-systems. The problem of different transformation properties can be remedied in two alternative ways. On the one hand, one can give up mass conservation in favour for

a fully relativistic description of matter. On the other hand, one may try to couple a low velocity Galilean limit system of the Maxwell equations to the classical, i.e. non-relativistic, balance equations of mixtures of matter.

In this work, we proceed with the second of the alternatives, since we aim at engineering applications and in particular electrochemical applications. As shown by [14], cf. also [17], there is not one unique Galilei limit of the Maxwell equations, but instead there are two distinct limits, i.e. the electric –or quasi-electrostatic– limit and the magnetic –or quasi-magnetostatic– limit. While coupling the electric limit to the balance equations of mass, momentum and energy seems most reasonable for electrochemical applications, the magnetic Galileo limit is more naturally related to magneto-hydrodynamics. We re-examine the derivation of Galilean limit systems of the Maxwell equations here, as we are not aware this has been carried out before for the case of singular surfaces. This way we can make sure that we do not miss relevant effects during coupling to the balances of matter later on or during the following derivation of constitutive equations. For each of the two Galileo limit cases considered in this work, there is one corresponding variant of the entropy principle in [9] such that coupling the general full set of Maxwell equations to the classical balance equations of matter and taking the Galilean limit after exploitation of the entropy principle yields the same results as obtained here. However, none of the two alternative variants of the entropy principle in [9] is capable to cover both Galilean limit cases equally well. It turns out that the application of the entropy principle here is much more straightforward compared to [9], as a re-definition of a combined inner energy of field and matter becomes unnecessary and a discussion of stability of the polarization relaxation does not arise.

The obtained constitutive equations differ between the two Galileo limit cases. As could be expected, polarization relaxation is only covered in the quasi-electrostatic case, whereas relaxation of magnetization is only present in the quasi-magnetostatic case. Moreover, the generalized driving forces for thermo-diffusion differ between the Galileo limits, as does the stress tensor.

We apply the geometrical setting and notation of [9] but neglected the elastic deformations, since these effects do not contribute to the questions discussed here. The results obtained here can be generalized in a save and straightforward manner to include elastic effects in the same way as in [9].

2 Notation

We consider a geometrical setup where locally an orientable surface S divides a domain $\Omega \subset \mathbb{R}^3$ into two subdomains $\Omega^\pm \subseteq \mathbb{R}^3$ with $S := \partial\Omega^+ \cap \partial\Omega^-$. The domain Ω , as well as the surface S may evolve in time. In addition to quantities defined in the domains Ω^+ or Ω^- , there are in general corresponding quantities on the surfaces S which in general do not coincide with the corresponding traces from the subdomains. As a convention, the same letters are used for these quantities, but the surface variables are indicated by an underset s .

We apply the convention of implicit summation over coordinate indices appearing twice. We indicate the Cartesian components of vectors and tensors by lowercase Latin indices, e.g., i, j , whereas at the surface S , we use uppercase Greek indices like e.g., Γ, Δ for the tangential components.

The tangential vectors are defined as the partial derivatives of the smooth bijective parametrization θ mapping from some open parameter domain to the surface S . In addition, we define the (unit) normal vector, and the metric tensor by

$$\boldsymbol{\tau}_{1/2} = \frac{\partial\theta(t, U^1, U^2)}{\partial U^{1/2}}, \quad \boldsymbol{\nu} = \frac{\boldsymbol{\tau}_1 \times \boldsymbol{\tau}_2}{|\boldsymbol{\tau}_1 \times \boldsymbol{\tau}_2|} \quad \text{and} \quad \boldsymbol{g} = [\boldsymbol{\tau}_1, \boldsymbol{\tau}_2]^T [\boldsymbol{\tau}_1, \boldsymbol{\tau}_2]. \quad (2.1)$$

As a convention, we chose the mapping θ such that ν is the inner normal of Ω^+ . For the matrix components of the metric tensor g , we use lower indices $g_{\Delta\Gamma}$ and, we use upper indices $g^{\Delta\Gamma}$ for the components of the inverse matrix of the metric. A vector \mathbf{V} defined on the surface can thus be written as $\mathbf{V} = V_\tau^\Delta \boldsymbol{\tau}_\Delta + V_\nu \boldsymbol{\nu}$, with the normal component by V_ν and the tangential components $V_\tau^\Delta = g^{\Gamma\Delta} \mathbf{V} \boldsymbol{\tau}_\Gamma$, for $\Delta = 1, 2$.

The *curvature tensor* $b_{\Delta\Gamma}$ of the surface S and the *Christoffel symbols* $\Gamma_{\Delta\Gamma}^\Sigma$ are defined by a decomposition of the derivatives of the tangential vectors into their tangential and normal components,

$$\frac{\partial \boldsymbol{\tau}_\Delta}{\partial U^\Gamma} = \Gamma_{\Delta\Gamma}^\Sigma \boldsymbol{\tau}_\Sigma + b_{\Delta\Gamma} \boldsymbol{\nu} \quad \text{for } \Gamma, \Delta = 1, 2. \quad (2.2)$$

Then, the mean curvature of S is $k_M = \frac{1}{2} b_{\Gamma\Delta} g^{\Gamma\Delta}$. Let $a : S \rightarrow \mathbb{R}$ be a scalar and $\mathbf{V} : S \rightarrow \mathbb{R}^3$ a vector field. Then, the covariant derivatives of the tangential components are defined as

$$a_{\parallel\Gamma} = \frac{\partial a}{\partial U^\Gamma}, \quad \text{for } \Gamma = 1, 2, \quad V_{\tau\parallel\Gamma}^\Delta = \frac{\partial V_\tau^\Delta}{\partial U^\Gamma} + \Gamma_{\Gamma\Sigma}^\Delta V_\tau^\Sigma \quad \text{for } \Gamma, \Delta = 1, 2. \quad (2.3)$$

Let v_s denote the velocity of the surface S . For a scalar $a : [0, t_{\text{end}}) \times S \rightarrow \mathbb{R}$, we define the time derivative

$$\partial_{t,\nu} a = \partial_t a - a_{\parallel\Delta} v_s^\Delta. \quad (2.4)$$

Let u be a generic function defined at least in one of the subdomains Ω^\pm . We denote the *trace* of u by

$$u^\pm(t, \mathbf{x}) = \lim_{\mathbf{x} \in \Omega^\pm \rightarrow \mathbf{x} \in S} u(t, \mathbf{x}). \quad (2.5)$$

whenever u is defined on this side of the surface, otherwise we set the corresponding trace to zero. We define the *jump* and the *mean value* of u at the surface S by

$$[[u]] = u^+ - u^-, \quad \bar{u} = \frac{1}{2}(u^+ + u^-). \quad (2.6)$$

3 Maxwell equations and their Galilei limits

The Maxwell equations for the electromagnetic field are most generally formulated such that time and space and all involved equations are properly combined to four-dimensional objects. Then, the equations satisfy the most fundamental symmetry principle, i.e. the principle of relativity, meaning that balance equations as well as constitutive equations remain invariant with respect to arbitrary observer transformations.

Here, 1+3 dimensional the Maxwell equations are formulated in a way following the classical work of Truesdell and Toupin [18], with the postulation of universally valid Maxwell–Lorentz aether relations. The underlying physical principle is the conservation of charge and magnetic flux. In this 1+3-dimensional setting, Maxwell–Lorentz aether relations are only invariant with respect to Lorentz transformations. The Galilean transformation is a good approximation of the Lorentz transformation in the limit of vanishing barycentric velocity, i.e., $v/c_0 \rightarrow 0$. However, the derivation of a Galilean limit system of the Maxwell equations is complicated by the fact that there are two different limit systems, cf. [14, 17].

3.1 General Maxwell equations

The (total) electric charge density n^e in each volume domain Ω^\pm , as well as n_s^e on the surface, satisfy local conservation equations, viz.

$$\partial_t n^e + \operatorname{div}(n^e \mathbf{v} + \mathbf{J}^e) = 0, \quad (3.1a)$$

$$\partial_{t,\nu} n_s^e + \left(n_s^e v_\tau^\Delta + J_\tau^e \right)_{\parallel \Delta} - 2k_M v_\nu n_s^e = -\llbracket n^e (v_\nu - v_\nu) + J_\nu^e \rrbracket. \quad (3.1b)$$

Here we split the electric current as $\mathbf{j}^e = n^e \mathbf{v} + \mathbf{J}^e$. We introduce the charge potential \mathbf{D} and the current potential \mathbf{H} by means of a formal solution of the charge balances (3.1), see [9, Appendix A]. Therefore, we have

$$n^e = \operatorname{div}(\mathbf{D}), \quad \mathbf{J}^e = -\partial_t \mathbf{D} - \mathbf{v} \operatorname{div}(\mathbf{D}) + \operatorname{curl}(\mathbf{H}), \quad (3.2a)$$

$$n_s^e = \llbracket \mathbf{D} \cdot \boldsymbol{\nu} \rrbracket, \quad \mathbf{J}_s^e = \boldsymbol{\nu} \times \llbracket \mathbf{H} - \mathbf{v} \times \mathbf{D} \rrbracket. \quad (3.2b)$$

The conservation of magnetic flux in the bulk and on the surface reads

$$0 = \operatorname{div}(\mathbf{B}), \quad 0 = \partial_t \mathbf{B} + \operatorname{curl}(\mathbf{E}), \quad (3.2c)$$

$$0 = \llbracket \mathbf{B} \cdot \boldsymbol{\nu} \rrbracket, \quad 0 = \boldsymbol{\nu} \times \llbracket \mathbf{E} + \mathbf{v} \times \mathbf{B} \rrbracket, \quad (3.2d)$$

where \mathbf{E} is the electric field. We postulate universal valid Maxwell–Lorentz aether relations, i.e. independent of the considered material there holds

$$\mathbf{D} = \varepsilon_0 \mathbf{E} \quad \text{and} \quad \mathbf{H} = \frac{1}{\mu_0} \mathbf{B}, \quad (3.3)$$

where the dielectric constant ε_0 and the magnetic constant μ_0 are related to the speed of light by $\varepsilon_0 \mu_0 = c_0^{-2}$. The remaining constitutive quantity is the electric flux density \mathbf{J}^e .

As an immediate consequence of the universal valid Maxwell–Lorentz aether relations (3.3) and charge conservation (3.1a), we conclude that the sum of the electric current and the displacement current is at any time t and location \mathbf{x} source free. This motivates the definition of a total current as

$$\mathbf{j} := \mathbf{j}^e + \varepsilon_0 \partial_t \mathbf{E} \quad \implies \quad \operatorname{div}(\mathbf{j}) = 0. \quad (3.4)$$

Implied balances. From Maxwell's equations (3.2), the following two more balance equations can be derived, cf. [15]. The balance of electromagnetic momentum reads in each subdomain Ω^\pm as well as on the surface S

$$\partial_t (\mathbf{D} \times \mathbf{B}) - \operatorname{div}(\boldsymbol{\sigma}^{\text{EM}}) = -n^e \mathbf{E} - (n^e \mathbf{v} + \mathbf{J}^e) \times \mathbf{B} \quad =: -\mathbf{k}, \quad (3.5a)$$

$$-\llbracket \mathbf{D} \times \mathbf{B} \rrbracket_{\nu} + \llbracket \boldsymbol{\sigma}^{\text{EM}} \boldsymbol{\nu} \rrbracket = -n_s^e \bar{\mathbf{E}} - \left(n_s^e \mathbf{v} + \mathbf{J}_s^e \right) \times \bar{\mathbf{B}} \quad =: -\mathbf{k}_s, \quad (3.5b)$$

where the right hand sides are the negative Lorentz force in the volume and on the surface, respectively. The Maxwell stress tensor in (3.5) is

$$\boldsymbol{\sigma}^{\text{EM}} = \mathbf{E} \otimes \mathbf{D} - \frac{1}{2} \mathbf{E} \cdot \mathbf{D} \mathbf{1} + \mathbf{H} \otimes \mathbf{B} - \frac{1}{2} \mathbf{H} \cdot \mathbf{B} \mathbf{1}, \quad (3.6)$$

where $\mathbf{1}$ denotes the identity matrix. The balance of electromagnetic energy reads

$$\frac{1}{2} \partial_t (\mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H}) + \operatorname{div}(\mathbf{E} \times \mathbf{H}) = -(n^e \mathbf{v} + \mathbf{J}^e) \cdot \mathbf{E} \quad =: -\pi, \quad (3.7a)$$

$$-\frac{1}{2} \llbracket (\mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H}) \rrbracket_{\nu} + \llbracket (\mathbf{E} \times \mathbf{H}) \cdot \boldsymbol{\nu} \rrbracket = -\left(n_s^e \mathbf{v} + \mathbf{J}_s^e \right) \cdot \bar{\mathbf{E}} \quad =: -\pi_s, \quad (3.7b)$$

where the right hand sides are the negative Joule heat in the volume and on the surface, respectively.

3.2 Polarization and magnetization

When considering a macroscopic non-relativistic continuum description of mixtures of charged matter, there is the *free charge* density n^F defined as a Galilean conserved quantity. In general, this free charge does not coincide with the previously introduced electric charge n^e . For example, n^F may solely represent the net charge of molecules in a mixture without taking into account the internal electronic structure. However, also this internal electronic structure in general has relevance for the overall electromagnetic field. To bridge this gap and represent these microscopic effects on the more macroscopic level, we introduce the *polarization charge density* n^P and the *polarization current density* \mathbf{J}^P as

$$n^e = n^F + n^P, \quad \mathbf{J}^e = \mathbf{J}^F + \mathbf{J}^P, \quad (3.8)$$

Conservation of the electric charge n^e and of the free charge n^F then also imply conservation of the polarization charge $n^P = n^e - n^F$. We introduce the vector of *polarization* \mathbf{P} and *Lorentz magnetization* \mathbf{M} by the same approach of formal solution to the conservation equations, viz.

$$n^P = -\operatorname{div}(\mathbf{P}), \quad \mathbf{J}^P = \partial_t \mathbf{P} + \mathbf{v} \operatorname{div}(\mathbf{P}) + \operatorname{curl}(\mathbf{M}), \quad (3.9a)$$

$$n_s^P = -\llbracket \mathbf{P} \rrbracket \cdot \boldsymbol{\nu}, \quad \mathbf{J}_s^P = \boldsymbol{\nu} \times \llbracket \mathbf{M} + \mathbf{v} \times \mathbf{P} \rrbracket. \quad (3.9b)$$

Not all of the introduced quantities so far are Galilean scalars, vectors or tensors, respectively. The transformation properties of these quantities are summarized in the supplementary material. Due to its importance in electrodynamics and for the upcoming constitutive modelling, we introduce the Galilean vectors of the *electromotive intensity* and the *magnetization*

$$\boldsymbol{\mathcal{E}} = \mathbf{E} + \mathbf{v} \times \mathbf{B}, \quad \boldsymbol{\mathcal{M}} = \mathbf{M} + \mathbf{v} \times \mathbf{P}. \quad (3.10)$$

The electric current then can be expressed as

$$\mathbf{j}^e = n^F \mathbf{v} + \mathbf{J}^F + \partial_t \mathbf{P} + \operatorname{curl}(\boldsymbol{\mathcal{M}} - \mathbf{v} \times \mathbf{P}). \quad (3.11)$$

For later use in the balance of inner energy, we verify that

$$\pi - \mathbf{k} \cdot \mathbf{v} = (\mathbf{J}^F + \mathbf{J}^P) \cdot \boldsymbol{\mathcal{E}} \quad (3.12a)$$

$$\pi_s - \mathbf{k}_s \cdot \mathbf{v}_s = (\mathbf{J}_s^F + \mathbf{J}_s^P) \cdot (\bar{\boldsymbol{\mathcal{E}}} + \mathbf{v}_s \times \bar{\boldsymbol{\mathcal{B}}}). \quad (3.12b)$$

3.3 Non-dimensional system and quasi-static Galilei limits

Non-dimensional form of the system. To write the model equations in non-dimensional form, we introduce characteristic reference values $t^{\text{ref}}, x^{\text{ref}}$ for the time and space coordinates. Velocity, is then scaled by the derived reference value $v^{\text{ref}} = x^{\text{ref}}/t^{\text{ref}}$. However, we remark that a different scaling of velocity might be more appropriate in a system coupled to diffusion of matter. We introduce reference values $E^{\text{ref}}, B^{\text{ref}}$ for the electric and magnetic field strength, respectively. Moreover, we use the elementary charge e_0 as reference value for charge and introduce T^{ref} and n_α^{ref} as reference values for the temperature and for number densities of particles in the volume domains, respectively.

Upon definition of the dimensionless constants

$$\beta = \sqrt{\frac{c_0 B^{\text{ref}}}{E^{\text{ref}}}}, \quad \lambda = \sqrt{\frac{\varepsilon_0 E^{\text{ref}}}{e_0 n^{\text{ref}} x^{\text{ref}}}}, \quad \kappa = \sqrt{\frac{e_0 c_0 B^{\text{ref}} x^{\text{ref}}}{k_B T^{\text{ref}}}}, \quad (3.13)$$

Table 1: Scaling of variables and constitutive functions in the bulk regions.

$\boldsymbol{x} = x^{\text{ref}} \cdot \check{\boldsymbol{x}},$	$t = t^{\text{ref}} \cdot \check{t},$	$\boldsymbol{v} = \frac{x^{\text{ref}}}{t^{\text{ref}}} \cdot \check{\boldsymbol{v}},$
$\boldsymbol{E} = E^{\text{ref}} \cdot \check{\boldsymbol{E}},$	$\boldsymbol{\mathcal{E}} = E^{\text{ref}} \cdot \check{\boldsymbol{\mathcal{E}}},$	$\boldsymbol{P} = \varepsilon_0 E^{\text{ref}} \cdot \check{\boldsymbol{P}},$
$\boldsymbol{B} = B^{\text{ref}} \cdot \check{\boldsymbol{B}},$	$\boldsymbol{\mathcal{M}} = \frac{1}{\mu_0} B^{\text{ref}} \cdot \check{\boldsymbol{\mathcal{M}}},$	$\boldsymbol{M} = \frac{1}{\mu_0} B^{\text{ref}} \cdot \check{\boldsymbol{M}},$
$n^{\text{F}} = e_0 n^{\text{ref}} \cdot \check{n}^{\text{F}},$	$\boldsymbol{J}^{\text{F}} = e_0 n^{\text{ref}} \frac{x^{\text{ref}}}{t^{\text{ref}}} \cdot \check{\boldsymbol{J}}^{\text{F}},$	$\boldsymbol{J}^{\text{e}} = e_0 n^{\text{ref}} \frac{x^{\text{ref}}}{t^{\text{ref}}} \cdot \check{\boldsymbol{J}}^{\text{e}},$
$\boldsymbol{\sigma}^{\text{EM}} = k_B T^{\text{ref}} n^{\text{ref}} \cdot \check{\boldsymbol{\sigma}}^{\text{EM}},$	$\boldsymbol{k} = k_B T^{\text{ref}} n^{\text{ref}} \frac{1}{x^{\text{ref}}} \cdot \check{\boldsymbol{k}},$	$\pi = k_B T^{\text{ref}} n^{\text{ref}} \frac{1}{t^{\text{ref}}} \cdot \check{\pi},$
$n_s^{\text{F}} = e_0 n_s^{\text{ref}} \cdot \check{n}_s^{\text{F}},$	$\boldsymbol{J}_s^{\text{F}} = e_0 n_s^{\text{ref}} \frac{x^{\text{ref}}}{t^{\text{ref}}} \cdot \check{\boldsymbol{J}}_s^{\text{F}},$	$\boldsymbol{J}_s^{\text{e}} = e_0 n_s^{\text{ref}} \frac{x^{\text{ref}}}{t^{\text{ref}}} \cdot \check{\boldsymbol{J}}_s^{\text{e}},$
	$\boldsymbol{k}_s = k_B T^{\text{ref}} n_s^{\text{ref}} \frac{1}{x^{\text{ref}}} \cdot \check{\boldsymbol{k}}_s,$	$\pi_s = k_B T^{\text{ref}} n_s^{\text{ref}} \frac{1}{t^{\text{ref}}} \cdot \check{\pi}_s,$

we obtain in the volume domains Ω^\pm the following dimensionless system

$$\lambda^2 \operatorname{div}(\check{\boldsymbol{E}} + \check{\boldsymbol{P}}) = \check{n}^{\text{F}}, \quad (3.14a)$$

$$-\lambda^2 \partial_t(\check{\boldsymbol{E}} + \check{\boldsymbol{P}}) + \lambda^2 \frac{c_0}{v^{\text{ref}}} \beta^2 \operatorname{curl}(\check{\boldsymbol{B}} - \check{\boldsymbol{M}}) = \check{n}^{\text{F}} \check{\boldsymbol{v}} + \check{\boldsymbol{J}}^{\text{F}}, \quad (3.14b)$$

$$\operatorname{div}(\check{\boldsymbol{B}}) = 0, \quad (3.14c)$$

$$\beta^2 \frac{v^{\text{ref}}}{c_0} \partial_t \check{\boldsymbol{B}} + \operatorname{curl}(\check{\boldsymbol{E}}) = 0. \quad (3.14d)$$

For the surface, we introduce an additional reference number density n_s^{ref} and relate it to the volume by the dimensionless constant

$$\delta = \frac{n_s^{\text{ref}}}{n^{\text{ref}} \lambda x^{\text{ref}}}. \quad (3.15)$$

Then the surface balances are in dimensionless form

$$\lambda [(\check{\boldsymbol{E}} + \check{\boldsymbol{P}}) \cdot \boldsymbol{\nu}] = \delta \check{n}_s^{\text{F}}, \quad (3.16a)$$

$$\lambda \boldsymbol{\nu} \times [\frac{c_0}{v^{\text{ref}}} \beta^2 (\check{\boldsymbol{B}} - \check{\boldsymbol{M}}) - \check{\boldsymbol{v}} \times (\check{\boldsymbol{E}} + \check{\boldsymbol{P}})] = \delta \check{\boldsymbol{J}}_s^{\text{F}}, \quad (3.16b)$$

$$[\check{\boldsymbol{B}} \cdot \boldsymbol{\nu}] = 0, \quad (3.16c)$$

$$\boldsymbol{\nu} \times [\check{\boldsymbol{E}} + \beta^2 \frac{v^{\text{ref}}}{c_0} \check{\boldsymbol{v}} \times \check{\boldsymbol{B}}] = 0. \quad (3.16d)$$

The balance of electromagnetic momentum reads in the volume domains and on the surface

$$\beta^2 \partial_t (\kappa^2 \lambda^2 \frac{v^{\text{ref}}}{c_0} \check{\boldsymbol{E}} \times \check{\boldsymbol{B}}) + \operatorname{div}(-\beta^2 \check{\boldsymbol{\sigma}}^{\text{EM}}) = -\beta^2 \check{\boldsymbol{k}}, \quad (3.17a)$$

$$-\beta^2 [\kappa^2 \lambda^2 \frac{v^{\text{ref}}}{c_0} \cdot (\check{\boldsymbol{E}} \times \check{\boldsymbol{B}}) \check{v}_\nu] + [\beta^2 \check{\boldsymbol{\sigma}}^{\text{EM}} \boldsymbol{\nu}] = -\lambda \delta \beta^2 \check{\boldsymbol{k}}_s. \quad (3.17b)$$

Here, the Maxwell stress tensor multiplied by β^2 , viz.

$$\beta^2 \check{\boldsymbol{\sigma}}^{\text{EM}} = \kappa^2 \lambda^2 \cdot \left(\check{\boldsymbol{E}} \otimes \check{\boldsymbol{E}} - \frac{1}{2} \check{\boldsymbol{E}} \cdot \check{\boldsymbol{E}} \mathbf{1} + \beta^4 (\check{\boldsymbol{B}} \otimes \check{\boldsymbol{B}} - \frac{1}{2} \check{\boldsymbol{B}} \cdot \check{\boldsymbol{B}} \mathbf{1}) \right) \quad (3.18)$$

contains terms independent of β^2 , as well as the Lorentz force and the Joule heat do, i.e.

$$\beta^2 \check{\mathbf{k}} = \kappa^2 \cdot \left(\check{n}^e \check{\mathbf{E}} + \beta^2 \frac{v^{\text{ref}}}{c_0} \check{\mathbf{J}}^e \times \check{\mathbf{B}} \right), \quad \beta^2 \check{\pi} = \kappa^2 \cdot \left(\check{n}^e \check{\mathbf{E}} \cdot \check{\mathbf{v}} + \check{\mathbf{J}}^e \cdot \check{\mathbf{E}} \right), \quad (3.19a)$$

$$\beta^2 \check{\mathbf{k}}_s = \kappa^2 \cdot \left(\check{n}_s^e \check{\mathbf{E}} + \beta^2 \frac{v^{\text{ref}}}{c_0} \left(\check{n}_s^e \check{\mathbf{v}} + \check{\mathbf{J}}_s^e \right) \times \check{\mathbf{B}} \right), \quad \beta^2 \check{\pi}_s = \kappa^2 \cdot \left(\check{n}_s^e \check{\mathbf{E}} \cdot \check{\mathbf{v}} + \check{\mathbf{J}}_s^e \cdot \check{\mathbf{E}} \right). \quad (3.19b)$$

The electromotive intensity and magnetization are

$$\check{\mathbf{E}} = \check{\mathbf{E}} + \beta^2 \frac{v^{\text{ref}}}{c_0} (\check{\mathbf{v}} \times \check{\mathbf{B}}), \quad \check{\mathcal{M}} = \check{\mathcal{M}} + \frac{v^{\text{ref}}}{c_0} \frac{1}{\beta^2} (\check{\mathbf{v}} \times \check{\mathbf{P}}), \quad (3.20)$$

The balance of electromagnetic energy reads

$$\frac{1}{2} \lambda^2 \kappa^2 \partial_t \left(\frac{1}{\beta^2} |\check{\mathbf{E}}|^2 + \beta^2 |\check{\mathbf{B}}|^2 \right) + \lambda^2 \kappa^2 \operatorname{div} \left(\check{\mathbf{E}} \times \check{\mathbf{B}} \right) = -\check{\pi}, \quad (3.21a)$$

$$-\frac{1}{2} \lambda \kappa^2 \left[\left(\frac{1}{\beta^2} |\check{\mathbf{E}}|^2 + \beta^2 |\check{\mathbf{B}}|^2 \right) v_\nu \right] + \lambda \kappa^2 \left[(\check{\mathbf{E}} \times \check{\mathbf{B}}) \cdot \boldsymbol{\nu} \right] = -\delta \check{\pi}_s, \quad (3.21b)$$

and the introduction of polarization and Lorentz magnetization imply for the electric current and the surface electric charge flux

$$\check{\mathbf{j}}^e = \check{n}^F \check{\mathbf{v}} + \check{\mathbf{J}}^F + \lambda^2 \partial_t \check{\mathbf{P}} + \lambda^2 \operatorname{curl} \left(\frac{c_0}{v^{\text{ref}}} \beta^2 \check{\mathcal{M}} - \check{\mathbf{v}} \times \check{\mathbf{P}} \right), \quad (3.22a)$$

$$\delta \check{\mathbf{J}}_s^e = \lambda \boldsymbol{\nu} \times \left[\frac{c_0}{v^{\text{ref}}} \beta^2 \check{\mathbf{B}} - \check{\mathbf{v}} \times \check{\mathbf{E}} \right]. \quad (3.22b)$$

Depending on the chosen characteristic reference values t^{ref} , x^{ref} , E^{ref} , B^{ref} , T^{ref} , n_α^{ref} and n_s^{ref} , the size of the dimensionless quantities may differ by several orders of magnitude, allowing considerable simplifications of the model equations. We consider in the following two alternative limiting cases for the parameter β , whereas we only assume for the remaining parameters λ , κ , ω , δ that they remain moderate in size. At this point, we only remark that later on, it is possible to analyze additional limit processes, like e.g. $\lambda \rightarrow 0$ what corresponds to the thin interface limit in electrochemical applications.

3.4 Quasi-electrostatic limit $\beta^2 \ll 1$

We assume that β is a small parameter, whereas $\frac{v^{\text{ref}}}{c_0}$ and the time derivative of \mathbf{B} remain bounded. In consequence, we obtain the equations of electrostatics for the electric field that read in dimensional form

$$\operatorname{div}(\varepsilon_0 \mathbf{E} + \mathbf{P}) = n^F, \quad [(\varepsilon_0 \mathbf{E} + \mathbf{P}) \cdot \boldsymbol{\nu}] = n_s^F, \quad (3.23a)$$

$$\operatorname{curl}(\mathbf{E}) = 0, \quad \boldsymbol{\nu} \times [\mathbf{E}] = 0. \quad (3.23b)$$

A constitutive equation for \mathbf{P} , which is independent of \mathbf{B} and \mathcal{M} , then allows for given free charge to obtain \mathbf{E} and \mathbf{P} from (3.23). The balance of electromagnetic momentum reduces to

$$-\operatorname{div}(\boldsymbol{\sigma}^{\text{EM}}) = -\mathbf{k}, \quad +[[\boldsymbol{\sigma}^{\text{EM}} \boldsymbol{\nu}]] = -\mathbf{k}_s, \quad (3.24)$$

with the Maxwell stress tensor depending only on \mathbf{E} , viz.

$$\boldsymbol{\sigma}^{\text{EM}} = \varepsilon_0 (\mathbf{E} \otimes \mathbf{E} - \frac{1}{2} |\mathbf{E}|^2 \mathbf{1}). \quad (3.25)$$

In this limit, the electromotive intensity is identical to the electric field. The magnetic field is not vanishing, only it does not have any effect on the Lorentz force, viz.

$$\mathcal{E} = \mathbf{E}, \quad \mathbf{k} = n^c \mathbf{E}, \quad \pi = n^c \mathbf{E} \cdot \mathbf{v} + \mathbf{J}^c \cdot \mathbf{E}, \quad (3.26a)$$

$$\underset{s}{\mathbf{k}} = n^c \underset{s}{\bar{\mathbf{E}}}, \quad \underset{s}{\pi} = n^c \underset{s}{\bar{\mathbf{E}}} \cdot \underset{s}{\mathbf{v}} + \underset{s}{\mathbf{J}^c} \cdot \underset{s}{\bar{\mathbf{E}}}. \quad (3.26b)$$

The Joule heat can not be evaluated from \mathbf{E} and \mathbf{P} alone, but also requires knowledge of \mathbf{B} . The remaining Maxwell's equations, in general together with a constitutive equation for \mathcal{M} , determine the magnetic flux density \mathbf{B} , i.e.,

$$\operatorname{div}(\mathbf{B}) = 0, \quad \partial_t(\varepsilon_0 \mathbf{E} + \mathbf{P}) + n^F \mathbf{v} + \mathbf{J}^F = \operatorname{curl}\left(\frac{1}{\mu_0} \mathbf{B} - \mathcal{M} + \mathbf{v} \times \mathbf{P}\right), \quad (3.27a)$$

$$\llbracket \mathbf{B} \cdot \boldsymbol{\nu} \rrbracket = 0, \quad \boldsymbol{\nu} \times \llbracket \mathbf{v} \times (\varepsilon_0 \mathbf{E} + \mathbf{P}) \rrbracket + \underset{s}{\mathbf{J}^F} = \boldsymbol{\nu} \times \llbracket \frac{1}{\mu_0} \mathbf{B} - \mathcal{M} + \mathbf{v} \times \mathbf{P} \rrbracket. \quad (3.27b)$$

The electric current and the surface current flux are then

$$\mathbf{j}^c = n^F \mathbf{v} + \mathbf{J}^F + \partial_t \mathbf{P} + \operatorname{curl}(\mathcal{M} - \mathbf{v} \times \mathbf{P}), \quad \underset{s}{\mathbf{J}^c} = \boldsymbol{\nu} \times \llbracket \frac{1}{\mu_0} \mathbf{B} - \mathbf{v} \times (\varepsilon_0 \mathbf{E}) \rrbracket. \quad (3.28)$$

3.5 Quasi-magnetostatic limit $\frac{1}{\beta^2} \ll 1$

Under the assumption that the derivatives of $\check{\mathbf{E}} + \check{\mathbf{P}}$ remain bounded, Maxwell's equations simplify in this limit to

$$\operatorname{curl}\left(\frac{1}{\mu_0} \mathbf{B} - \mathcal{M}\right) = n^F \mathbf{v} + \mathbf{J}^F, \quad \boldsymbol{\nu} \times \llbracket \frac{1}{\mu_0} \mathbf{B} - \mathcal{M} \rrbracket = \underset{s}{\mathbf{J}^F}, \quad (3.29a)$$

$$\operatorname{div}(\mathbf{B}) = 0, \quad \llbracket \mathbf{B} \cdot \boldsymbol{\nu} \rrbracket = 0. \quad (3.29b)$$

A constitutive equation for \mathcal{M} , which is independent of \mathcal{E} and \mathbf{P} , then allows for given free current to obtain \mathbf{B} and \mathcal{M} from (3.29). The balance of electromagnetic momentum reduces to

$$-\operatorname{div}(\boldsymbol{\sigma}^{\text{EM}}) = -\mathbf{k}, \quad +\llbracket \boldsymbol{\sigma}^{\text{EM}} \boldsymbol{\nu} \rrbracket = -\underset{s}{\mathbf{k}}, \quad (3.30)$$

with the Maxwell stress tensor depending only on \mathbf{B} , viz.

$$\boldsymbol{\sigma}^{\text{EM}} = \frac{1}{\mu_0} (\mathbf{B} \otimes \mathbf{B} - \frac{1}{2} |\mathbf{B}|^2 \mathbf{1}). \quad (3.31)$$

In the quasi-magnetostatic limit, the magnetization is identical to the Lorentz magnetization. The electric field does not vanish, only it does not have any effect on the Lorentz force and the Joule heat is negligible, viz.

$$\mathcal{M} = \mathcal{M}, \quad \mathbf{k} = (n^c \mathbf{v} + \mathbf{J}^c) \times \mathbf{B}, \quad \pi - \mathbf{k} \cdot \mathbf{v} = \mathbf{J}^c \cdot (\mathbf{v} \times \mathbf{B}), \quad (3.32a)$$

$$\underset{s}{\mathbf{k}} = (\underset{s}{n^c} \underset{s}{\mathbf{v}} + \underset{s}{\mathbf{J}^c}) \times \underset{s}{\bar{\mathbf{B}}}, \quad \underset{s}{\pi} - \underset{s}{\mathbf{k}} \cdot \underset{s}{\mathbf{v}} = \underset{s}{\mathbf{J}^c} \cdot (\underset{s}{\mathbf{v}} \times \underset{s}{\bar{\mathbf{B}}}). \quad (3.32b)$$

The Lorentz force can not be evaluated from \mathbf{B} and \mathcal{M} alone, but also requires knowledge of \mathbf{E} . The remaining Maxwell's equations, together with a constitutive equation for \mathbf{P} determine the electric field, i.e.

$$\partial_t \mathbf{B} + \operatorname{curl}(\mathbf{E}) = 0, \quad \boldsymbol{\nu} \times \llbracket \mathbf{E} + \mathbf{v} \times \mathbf{B} \rrbracket = 0, \quad (3.33a)$$

$$\operatorname{div}(\varepsilon_0 \mathbf{E} + \mathbf{P}) = n^F, \quad \llbracket (\varepsilon_0 \mathbf{E} + \mathbf{P}) \cdot \boldsymbol{\nu} \rrbracket = \underset{s}{n^F}. \quad (3.33b)$$

The electric current and the surface current flux are

$$\mathbf{j}^c = n^F \mathbf{v} + \mathbf{J}^F + \partial_t \mathbf{P} + \operatorname{curl}(\mathcal{M}), \quad \underset{s}{\mathbf{J}^c} = \boldsymbol{\nu} \times \llbracket \frac{1}{\mu_0} \mathbf{B} \rrbracket. \quad (3.34)$$

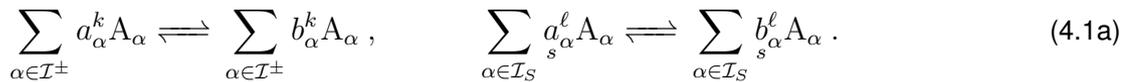
4 Balance equations of Galilean electro-thermodynamics

The Galilean limit systems of electromagnetics can now be consistently coupled to classical, i.e., non-relativistic balance equations for charged mixtures of matter. We consider partial mass balances for each of the constituents of the mixture, a single momentum balance of the mixture and an energy balance of matter.

4.1 Description of Reacting Mixtures

We use different index sets \mathcal{I}^\pm to refer to the constituents of a mixture in Ω^\pm and the index set \mathcal{I}_S for the constituents on the surface S . We apply the non-restrictive assumption that the sets \mathcal{I}^\pm are disjoint, i.e., $\mathcal{I}^+ \cap \mathcal{I}^- = \emptyset$. All constituents of the subdomains Ω^\pm are assumed to be also constituents on the surface S , but there may be some additional constituents that are exclusively present on S . Thus, we have $\mathcal{I}^\pm \subseteq \mathcal{I}_S$.

There may be several chemical reactions among the bulk constituents, as well as chemical reactions on the surface. Picking some indices k, ℓ , then these reactions in the bulk or surface may be written in the general form



where A_α is used as a notation to refer to the different constituents. The constants a_α^k, b_α^k are positive integers and $\gamma_\alpha^k := b_\alpha^k - a_\alpha^k$ denote the stoichiometric coefficients of the reactions. The net reaction rate is R^k , where reactions in the direction from left to right are counted positive.

Each constituent has the (atomic) mass m_α , for $\alpha \in \mathcal{I}^\pm$ or $\alpha \in \mathcal{I}_S$, and the net charge $z_\alpha e_0$, where z_α is the charge number of the constituent. Since charge and mass have to be conserved by each single reaction in the bulk and on the surface, we have

$$\sum_{\alpha \in \mathcal{I}^\pm} z_\alpha \gamma_\alpha^k = 0 \quad \text{and} \quad \sum_{\alpha \in \mathcal{I}^\pm} m_\alpha \gamma_\alpha^k = 0 \quad (4.2a)$$

$$\sum_{\alpha \in \mathcal{I}_S} z_\alpha \gamma_\alpha^\ell = 0 \quad \text{and} \quad \sum_{\alpha \in \mathcal{I}_S} m_\alpha \gamma_\alpha^\ell = 0 \quad (4.2b)$$

To describe the thermodynamic state of the mixture, we use in the volume domains the inner energy density ρu , the particle number densities n_α and partial velocities \mathbf{v}_α for $\alpha \in \mathcal{I}^\pm$. On the surface, the surface inner energy density $\rho_s u_s$, and the number densities and partial velocities of the surface constituents are n_α and \mathbf{v}_α for $\alpha \in \mathcal{I}_S$. Multiplication of the number densities by m_α gives the partial mass densities

$$\rho_\alpha = m_\alpha n_\alpha, \quad \rho_\alpha = m_\alpha n_\alpha. \quad (4.3)$$

The mass density and the barycentric velocity of the mixture are defined by

$$\rho = \sum_{\alpha \in \mathcal{I}^\pm} \rho_\alpha, \quad \mathbf{v} = \frac{1}{\rho} \sum_{\alpha \in \mathcal{I}^\pm} \rho_\alpha \mathbf{v}_\alpha, \quad (4.4a)$$

$$\rho_s = \sum_{\alpha \in \mathcal{I}_S} \rho_\alpha, \quad \mathbf{v}_s = \frac{1}{\rho_s} \sum_{\alpha \in \mathcal{I}_S} \rho_\alpha \mathbf{v}_\alpha. \quad (4.4b)$$

The free charge density and free current are defined as

$$n^F = e_0 \sum_{\alpha \in \mathcal{I}^\pm} z_\alpha n_\alpha, \quad \mathbf{J}^F = e_0 \sum_{\alpha \in \mathcal{I}^\pm} z_\alpha \mathbf{J}_\alpha, \quad (4.5a)$$

$$n_s^F = e_0 \sum_{\alpha \in \mathcal{I}_S} z_\alpha n_s^\alpha, \quad \mathbf{J}_s^F = e_0 \sum_{\alpha \in \mathcal{I}_S} z_\alpha \mathbf{J}_s^\alpha. \quad (4.5b)$$

4.2 Balance Equations

Partial mass balances. In each of the subdomains Ω^\pm as well as on the surface S , the partial mass balances are

$$\partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha \mathbf{v} + \mathbf{J}_\alpha) = \sum_k m_\alpha \gamma_\alpha^k R^k \quad \text{for } \alpha \in \mathcal{I}^\pm, \quad (4.6a)$$

$$\partial_{t,\nu} \rho_\alpha + (\rho_\alpha v_s^\Delta + J_{s,\tau}^\Delta)_{\|\Delta} - 2k_M v_\nu \rho_\alpha = \sum_\ell m_\alpha \gamma_\alpha^\ell R^\ell - \llbracket \rho_\alpha (v_\nu - v_\nu) + \mathbf{J}_\alpha \cdot \boldsymbol{\nu} \rrbracket \quad \text{for } \alpha \in \mathcal{I}_S. \quad (4.6b)$$

The (non-convective) bulk and surface diffusion flux \mathbf{J}_α and \mathbf{J}_s^α with respect to the barycentric velocity are defined as

$$\mathbf{J}_\alpha = \rho_\alpha (\mathbf{v}_\alpha - \mathbf{v}), \quad \text{implying} \quad \sum_{\alpha \in \mathcal{I}^\pm} \mathbf{J}_\alpha = 0, \quad (4.7a)$$

$$\mathbf{J}_s^\alpha = \rho_\alpha (\mathbf{v}_s^\alpha - \mathbf{v}), \quad \text{implying} \quad \sum_{\alpha \in \mathcal{I}_S} \mathbf{J}_s^\alpha = 0. \quad (4.7b)$$

The partial mass balances can be combined to derive bulk and surface conservation laws for the total mass density of the mixture and for the free charge.

Balance of momentum. In the absence of electromagnetic fields, the momentum density of the mixture with respect to the barycentric velocity is $\rho \mathbf{v}$. We postulate that in the absence of gravitation the total momentum of matter and electromagnetic field is a conserved quantity. In the Galilean limits of the Maxwell equations, the Maxwell stress $\boldsymbol{\sigma}^{\text{EM}}$ equals the negative Lorentz force, while the electromagnetic momentum density is negligible small. We introduce the *total stress tensor* $\boldsymbol{\Sigma}$ containing $\boldsymbol{\sigma}^{\text{EM}}$. Then in either of the Galilean limit cases, the total momentum balances of matter and electromagnetic field read in Ω^\pm and on S

$$\partial_t(\rho \mathbf{v}) + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v} - \boldsymbol{\Sigma}) = \rho \mathbf{f}, \quad (4.8a)$$

$$\partial_{t,\nu}(\rho v_s^i) + (\rho v_s^i v_s^\Delta - \sigma_s^{i\Delta})_{\|\Delta} - 2k_M v_\nu \rho v_s^i = \rho f_s^i - \llbracket \rho v_s^i (v_\nu - v_\nu) - \Sigma^{ij} \nu_j \rrbracket, \quad (4.8b)$$

where \mathbf{f} and \mathbf{f}_s are due to gravitation. The *surface momentum flux* $\boldsymbol{\sigma}_s$ is decomposed into its normal and tangential components

$$\boldsymbol{\sigma}_s^{i\Delta} = S^{\Gamma\Delta} \tau_\Gamma^i + S^\Delta \nu^i. \quad (4.9)$$

The tensor with the components $S^{\Gamma\Delta}$ is denoted as *surface stress tensor* and the vector with the components S^Δ is the *normal stress vector*. We neglect internal spin. Given the symmetry of the

Maxwell stress tensor due to the Maxwell–Lorentz aether relations, this implies symmetry of the total stress tensors and vanishing of the normal surface stress [15], i.e., the assumption implies for $i, j = 1, 2, 3$ and $\Gamma, \Delta = 1, 2$

$$\Sigma^{ij} = \Sigma^{ji}, \quad S^{\Gamma\Delta} = S^{\Delta\Gamma} \quad \text{and} \quad S^\Delta = 0. \quad (4.10)$$

From this balances, several different balances for the momentum $\rho \mathbf{v}$ can be derived, depending on which forces should be accounted for on the right hand side. Subtracting from (4.8) the momentum balance (3.24) in the quasi-electrostatic limit, or (3.30) in the quasi-magnetostatic limit, then yields the momentum balance equations of matter with the Lorentz force \mathbf{k} , respective \mathbf{k}_s , on the right hand side. In addition to the Lorentz force, one might also want to track *Kelvin polarization force*, *electrostrictive force*, or *Korteweg-Helmholtz force* explicitly in the balances, cf. [13, Sect. 3.2], such that the stress tensor then needs to be modified accordingly.

Balance of inner energy. The energy of matter consists of the *inner energy* density ρu and the *kinetic energy* density $\rho |\mathbf{v}|^2$. The balance equations of mass and momentum of matter imply the balances of kinetic energy in Ω^\pm and on S . Moreover, we postulate that in the absence of gravitation the *total energy* of matter and electromagnetic field is a conserved quantity. This implies the inner energy balances in Ω^\pm and on S as shown in Appendix A.1, viz.

$$\partial_t \rho u + \operatorname{div}(\rho u \mathbf{v} + \mathbf{Q}) = \pi - \mathbf{k} \cdot \mathbf{v} + \operatorname{div}(\mathbf{E} \times \mathbf{M}) + (\Sigma - \sigma^{\text{EM}}) : \nabla \mathbf{v}. \quad (4.11a)$$

$$\begin{aligned} \partial_{t,\nu} \rho u + \left(\rho u \right)_{s s} v_{s \tau}^\Delta + q_{s s}^\Delta \Big|_{\Delta} - 2k_M v_{s s} \rho u = \pi_s - \mathbf{k}_s \cdot \mathbf{v}_s + \left[(\mathbf{E} \times \mathbf{M}) \cdot \boldsymbol{\nu} \right] + \sigma_s^{i\Delta} v_{s s}^i \Big|_{\Delta} \quad (4.11b) \\ - \left[\rho u (v_\nu - v_{s\nu}) + \mathbf{Q} \cdot \boldsymbol{\nu} \right] \\ - \left[\frac{1}{2} \rho |\mathbf{v} - \mathbf{v}_s|^2 (v_\nu - v_{s\nu}) - (\Sigma - \sigma^{\text{EM}})(\mathbf{v} - \mathbf{v}_s) \cdot \boldsymbol{\nu} \right]. \end{aligned}$$

We can write $\mathbf{Q} = \mathbf{q} + \mathbf{E} \times \mathbf{M}$, such that \mathbf{q} coincides with the heat flux in the balance of inner and kinetic energy when the heat production is given by the Joule heat. Using the particular form of the Lorentz force and the Joule heat in quasi-electrostatic limit, we obtain for the inner energy balance

$$\begin{aligned} \partial_t \rho u + \operatorname{div}(\rho u \mathbf{v} + \mathbf{Q}) = \mathbf{J}^{\text{F}} \cdot \mathbf{E} + \left(\Sigma - \sigma^{\text{EM}} - \mathbf{E} \otimes \mathbf{P} + (\mathbf{E} \cdot \mathbf{P}) \mathbf{1} \right) : \nabla \mathbf{v} \\ + \left(\partial_t \mathbf{P} + (\mathbf{v} \cdot \nabla) \mathbf{P} \right) \cdot \mathbf{E}, \quad (4.12a) \end{aligned}$$

$$\begin{aligned} \partial_{t,\nu} (\rho u) + \left(\rho u \right)_{s s} v_{s \tau}^\Delta + q_{s s}^\Delta \Big|_{\Delta} - 2k_M v_{s s} \rho u = \mathbf{J}_s^{\text{F}} \cdot \bar{\mathbf{E}} + \sigma_s^{i\Delta} v_{s s}^i \Big|_{\Delta} \quad (4.12b) \\ - \left[\left(\rho u + \frac{1}{2} \rho |\mathbf{v} - \mathbf{v}_s|^2 \right) (v_\nu - v_{s\nu}) + \mathbf{Q} \cdot \boldsymbol{\nu} \right] \\ + \left[(\mathbf{v} - \mathbf{v}_s) \cdot (\Sigma - \sigma^{\text{EM}} - \mathbf{E} \otimes \mathbf{P} + (\mathbf{E} \cdot \mathbf{P}) \mathbf{1}) \cdot \boldsymbol{\nu} \right]. \end{aligned}$$

On the other hand, we get in the quasi-magnetostatic limit from the explicit Lorentz force and Joule heat

$$\begin{aligned} \partial_t \rho u + \operatorname{div}(\rho u \mathbf{v} + \mathbf{Q}) = \mathbf{J}^{\text{F}} \cdot (\mathbf{v} \times \mathbf{B}) + \left(\Sigma - \sigma^{\text{EM}} + \mathbf{M} \otimes \mathbf{B} - (\mathbf{M} \cdot \mathbf{B}) \mathbf{1} \right) : \nabla \mathbf{v} \\ - \left(\partial_t \mathbf{B} + (\mathbf{v} \cdot \nabla) \mathbf{B} \right) \cdot \mathbf{M}, \quad (4.13a) \end{aligned}$$

$$\begin{aligned}
\partial_{t,\nu}(\rho u) + (\rho u v_{\tau}^{\Delta} + q^{\Delta})_{\parallel\Delta} - 2k_M v_{\nu} \rho u &= \mathbf{J}^F \cdot (\mathbf{v} \times \bar{\mathbf{B}}) + \sigma_s^{i\Delta} v_{\parallel\Delta}^i \\
&- \left[\left(\rho u + \frac{1}{2} \rho |\mathbf{v} - \mathbf{v}_s|^2 \right) (v_{\nu} - v_{\nu s}) + \mathbf{Q} \cdot \boldsymbol{\nu} \right] \\
&+ \left[(\mathbf{v} - \mathbf{v}_s) \cdot (\boldsymbol{\Sigma} - \boldsymbol{\sigma}^{\text{EM}} + \mathbf{M} \otimes \mathbf{B} - (\mathbf{M} \cdot \mathbf{B}) \mathbf{1}) \cdot \boldsymbol{\nu} \right].
\end{aligned} \tag{4.13b}$$

5 Constitutive Equations for the quasi-electrostatic limit

In the quasi-electrostatic limit, the coupled electro-thermodynamic system consists of (3.23), (4.6), (4.8) and (4.12). To close the coupled system, additional constitutive relations are needed. These can be obtained from the application of an entropy principle like described in [9]. Because it allows a straightforward derivation of the entropy production in the desired form, we assume constitutive functions of the entropy densities of the form

$$\rho\eta = \tilde{\rho\eta}(\rho u, (\rho_{\alpha})_{\alpha \in \mathcal{I}^{\pm}}, \mathbf{P}), \quad \rho\eta = \tilde{\rho\eta}(\rho u, (\rho_{\alpha})_{\alpha \in \mathcal{I}_S}). \tag{5.1a}$$

In principle, it would also be possible to include a dependence of $\rho\tilde{\eta}$ on \mathcal{M} , such that by application of the entropy principle one more constitutive equation could be obtained which then would allow to solve (3.27) and to evaluate the electric current \mathbf{j}^e . In the quasi-electrostatic limit however, all explicit dependence of the system (3.23), (4.6), (4.8) and (4.12) on \mathbf{B} and \mathcal{M} was removed due to the asymptotic smallness of those terms. The application of the entropy principle builds on this system of equations and therefore it should not reintroduce asymptotically non-negligibly dependencies on \mathbf{B} and \mathcal{M} . Moreover, terms in the entropy production depending on \mathbf{B} and \mathcal{M} would be in the same asymptotic order as the terms that have been neglected in the system (3.23), (4.6), (4.8) and (4.12). Therefore, the value of constitutive equations based on such small terms in the entropy production must be questionable. Instead, it seems more advisable to use a constitutive equation relating \mathbf{B} and \mathcal{M} , which were derived from another source, which might well be the complementary quasi-magnetostatic limit in Sect. 6.

The (absolute) temperature T, T_s and the chemical potentials $\mu_{\alpha}, \mu_{\alpha s}$ are defined as

$$\frac{1}{T} = \frac{\partial \tilde{\rho\eta}}{\partial \rho u}, \quad \frac{\mu_{\alpha}}{T} = - \frac{\partial \tilde{\rho\eta}}{\partial \rho_{\alpha}}, \tag{5.2a}$$

$$\frac{1}{T_s} = \frac{\partial \tilde{\rho\eta}}{\partial \rho u_s}, \quad \frac{\mu_{\alpha s}}{T_s} = - \frac{\partial \tilde{\rho\eta}}{\partial \rho_{\alpha s}}. \tag{5.2b}$$

For the construction of constitutive equations, it is often beneficial to use the temperature T resp. T_s as an independent variable, instead of the inner energy density. We thus introduce the *free energy* densities $\rho\psi$ and $\rho\psi_s$ by means of Legendre transformation of the entropy density $\rho\eta$, viz.

$$\rho\psi = \rho u - T \rho\eta, \quad \rho\psi_s = \rho u_s - T_s \rho\eta_s. \tag{5.3}$$

For the free energy density and the entropy density, we thus have representations as functions of the temperature as

$$\rho\psi = \check{\rho\psi}(T, (\rho_{\alpha})_{\alpha \in \mathcal{I}^{\pm}}, \mathbf{P}), \quad \rho\psi_s = \hat{\rho\psi}_s(T_s, (\rho_{\alpha s})_{\alpha \in \mathcal{I}_S}), \tag{5.4}$$

and in analogous way for inner energy and entropy. From the construction (5.3) and the definition of temperature according to (5.2), we get the well known thermodynamic relations

$$\frac{\partial \rho \check{\psi}}{\partial T} = -\rho \check{\eta}, \quad \frac{\partial}{\partial T} \left(\frac{\rho \check{\psi}}{T} \right) = -\frac{\rho \check{u}}{T^2}, \quad (5.5a)$$

$$\frac{\partial \rho \hat{\psi}}{\partial T} = -\rho \hat{\eta}, \quad \frac{\partial}{\partial T} \left(\frac{\rho \hat{\psi}}{T} \right) = -\frac{\rho \hat{u}}{T^2}. \quad (5.5b)$$

5.1 Constitutive Relations for the Bulk

To determine the entropy production in a straightforward manner, chain rule is applied to the time derivative of $\rho \tilde{\eta}$ and the partial mass balances (4.6) and the inner energy balance (4.12) are applied. Then, the choice of the entropy flux fixes the entropy production. Nevertheless, the entropy production can still be rewritten in such a way that is most suitable for the derivation of constitutive relations. We choose the entropy flux as $\phi = \frac{Q}{T} - \sum_{\alpha \in \mathcal{I}} \frac{\mu_\alpha}{T} \mathbf{J}_\alpha$. Moreover, we define the viscous stress tensor and the symmetric velocity gradient as

$$\mathcal{T} = \Sigma - \sigma^{\text{EM}} - \left(\rho u - T \rho \tilde{\eta} - \mathbf{E} \cdot \mathbf{P} - \sum_{\alpha \in \mathcal{I}^\pm} \rho_\alpha \mu_\alpha \right) \mathbf{1} - \frac{1}{2} (\mathbf{E} \otimes \mathbf{P} + \mathbf{P} \otimes \mathbf{E}), \quad (5.6a)$$

$$\mathcal{D} = \frac{1}{2} (\nabla \mathbf{v} + \nabla \mathbf{v}^T). \quad (5.6b)$$

To account in the derivation of the entropy production for the constraint (4.7) on the mass fluxes, we choose in each subdomain one designated constituent as a reference and denote these constituents by A_{0-} , A_{0+} , respectively. Moreover, we use a symmetry condition which originates from the transformation properties of the thermodynamic fields, cf. [9, Appendix B]. Then, we obtain the entropy production as the sum of binary products, viz.

$$\begin{aligned} 0 \leq \xi &= \underbrace{\frac{1}{T} (\mathcal{T} - \frac{1}{3} \text{trace}(\mathcal{T}) \mathbf{1}) : (\mathcal{D} - \frac{1}{3} \text{trace}(\mathcal{D}) \mathbf{1})}_{=\xi_{SV}} + \underbrace{\frac{1}{3T} \text{trace}(\mathcal{T}) \cdot \text{trace}(\mathcal{D})}_{\xi_{VV}} \\ &+ \underbrace{Q \cdot \nabla \left(\frac{1}{T} \right) - \sum_{\alpha \in \mathcal{I}^\pm \setminus \{A_{0\pm}\}} \mathbf{J}_\alpha \cdot \left(\nabla \left(\frac{\mu_\alpha}{T} - \frac{\mu_{0\pm}}{T} \right) - \frac{1}{T} \left(\frac{z_\alpha e_0}{m_\alpha} - \frac{z_{0\pm} e_0}{m_{0\pm}} \right) \mathbf{E} \right)}_{=\xi_{TD}} \\ &+ \underbrace{\frac{1}{T} \sum_k \left(- \sum_{\alpha \in \mathcal{I}^\pm} \gamma_\alpha^k m_\alpha \mu_\alpha \right) \cdot R^k}_{\xi_R} + \underbrace{\left(\frac{\partial \rho \tilde{\eta}}{\partial \mathbf{P}} + \frac{1}{T} \mathbf{E} \right) \cdot \left(\partial_t \mathbf{P} + (\mathbf{v} \cdot \nabla) \mathbf{P} - \frac{1}{2} (\nabla \mathbf{v} - \nabla \mathbf{v}^T) \mathbf{P} \right)}_{\xi_P}. \end{aligned} \quad (5.7)$$

We can identify five dissipation mechanisms related to their specific entropy production: shear viscosity ξ_{SV} , volume viscosity ξ_{VV} , (bulk-)reactions ξ_R , thermodiffusion ξ_{TD} and polarization ξ_P . For each dissipation mechanism, we apply closure relations to obtain the constitutive equations.

Thermodiffusion: For the heat flux and the mass fluxes, we choose a linear relation with cross effects. We choose coefficients κ , L_β , $M_{\alpha\beta}$ such that the coefficient matrix is symmetric and positive definite. In particular, the heat conductivity κ and the mobility matrix M are symmetric and positive

definite. We set for $\alpha \in \mathcal{I}^\pm \setminus \{A_{0\pm}\}$

$$\mathbf{Q} = -\frac{\kappa}{T^2} \nabla T - \sum_{\beta \in \mathcal{I}^\pm \setminus \{A_{0\pm}\}} L_\beta \left(\nabla \left(\frac{\mu_\beta}{T} - \frac{\mu_{0\pm}}{T} \right) - \frac{1}{T} \left(\frac{z_\beta e_0}{m_\beta} - \frac{z_{0\pm} e_0}{m_{0\pm}} \right) \mathbf{E} \right), \quad (5.8a)$$

$$\mathbf{J}_\alpha = -\frac{L_\alpha}{T^2} \nabla T - \sum_{\beta \in \mathcal{I}^\pm \setminus \{A_{0\pm}\}} M_{\alpha\beta} \left(\nabla \left(\frac{\mu_\beta}{T} - \frac{\mu_{0\pm}}{T} \right) - \frac{1}{T} \left(\frac{z_\beta e_0}{m_\beta} - \frac{z_{0\pm} e_0}{m_{0\pm}} \right) \mathbf{E} \right). \quad (5.8b)$$

Reactions: For simplicity, we neglected cross effects between the different chemical reactions. We choose positive coefficients A^k, R_0^k and apply a nonlinear closure relation to obtain for any of the reactions in the volume domains

$$R^k = R_0^k \left(1 - \exp \left(\frac{A^k}{k_B T} \sum_{\alpha \in \mathcal{I}^\pm} \gamma_\alpha^k m_\alpha \mu_\alpha \right) \right). \quad (5.9)$$

Polarization: We choose a linear closure relation with the relaxation time $\tau^P \geq 0$ of polarization to obtain

$$\mathbf{E} + T \frac{\partial \rho \tilde{\eta}}{\partial \mathbf{P}} = \frac{\tau^P}{\varepsilon_0} \left(\partial_t \mathbf{P} + (\nabla \cdot \mathbf{v}) \mathbf{P} - \frac{1}{2} (\nabla \mathbf{v} - \nabla \mathbf{v}^T) \mathbf{P} \right). \quad (5.10)$$

Viscosity: Linear relations for the volume viscosity and for the shear viscosity with phenomenological coefficients η_b, η_s that satisfy $(\eta_b + \frac{2}{3}\eta_s) > 0$ and $\eta_s > 0$ yield

$$\mathcal{T} = \eta_b \operatorname{div}(\mathbf{v}) \mathbf{1} + \eta_s (\nabla \mathbf{v} + (\nabla \mathbf{v})^T). \quad (5.11)$$

This implies the constitutive equation for the symmetric stress tensor

$$\Sigma - \sigma^{\text{EM}} = \mathcal{T} + \left(\rho u - T \rho \tilde{\eta} - \mathbf{E} \cdot \mathbf{P} - \sum_{\alpha \in \mathcal{I}^\pm} \rho_\alpha \mu_\alpha \right) \mathbf{1} + \frac{1}{2} (\mathbf{E} \otimes \mathbf{P} + \mathbf{P} \otimes \mathbf{E}). \quad (5.12)$$

5.2 Constitutive Relations for the Surface

We proceed in analogous manner as in the volume and choose the surface entropy flux as $\phi_s =$

$\frac{q_s}{T_s} - \sum_{\alpha \in \mathcal{I}_S} \frac{\mu_\alpha}{T_s} \mathbf{J}_\alpha$. We define the tensors \mathcal{T} and \mathcal{D} with the components

$$\mathcal{T}_s^{\Delta\Gamma} = S^{\Gamma\Delta} - \left(\rho u - T_s \rho \tilde{\eta} - \sum_{\alpha \in \mathcal{I}_S} \mu_\alpha \rho_\alpha \right) g_s^{\Delta\Gamma}, \quad (5.13a)$$

$$\mathcal{D}_s^{\Delta\Gamma} = \frac{1}{2} (g_{\Gamma\Lambda} v_{s\tau||\Delta}^\Lambda + g_{\Delta\Lambda} v_{s\tau||\Gamma}^\Lambda) - b_{\Gamma\Delta} v_{s\nu}. \quad (5.13b)$$

Moreover, we choose one designated constituent $A_0 \in \mathcal{I}_S$ on the surface. Then we obtain the surface entropy production as a sum of binary products, viz.

$$\begin{aligned}
0 \leq \xi_s &= \underbrace{\frac{1}{T_s} \left[\mathcal{T}^{\Delta\Gamma} \right] \cdot \left(\mathcal{D}_{\Delta\Gamma} \right)}_{=\xi_s^{\mathcal{T}\nabla}} - \underbrace{\frac{1}{T_s} \sum_{\ell} \left(\sum_{\beta \in \mathcal{I}_S} \gamma_{\beta}^{\ell} m_{\beta} \mu_{\beta} \right) \cdot R_s^{\ell}}_{\xi_s^R} \\
&\quad + \underbrace{q_s^{\Delta} \cdot \left(\frac{1}{T_s} \right)_{\parallel\Delta} - \sum_{\alpha \in \mathcal{I}_S \setminus \{A_0\}} J_{s,\alpha,\tau}^{\Delta} \cdot \left(\left(\frac{\mu_{\alpha}}{T_s} - \frac{\mu_0}{T_s} \right)_{\parallel\Delta} - \frac{1}{T_s} \left(\frac{z_{\alpha} e_0}{m_{\alpha}} - \frac{z_0 e_0}{m_0} \right) g_{\Delta\Gamma} \bar{\mathbf{E}}_{\tau}^{\Gamma} \right)}_{=\xi_{TD}^{\mathcal{T}}} \\
&\quad + \underbrace{\left[\left(Q_{\nu} + (T \rho \tilde{\eta} + \sum_{\alpha \in \mathcal{I}^{\pm}} \rho_{\alpha} \mu_{\alpha}) (v_{\nu} - v_{\nu}) \right) \cdot \left(\frac{1}{T} - \frac{1}{T_s} \right) \right]}_{=\xi_H^{\mathcal{V}}} \\
&\quad + \underbrace{\frac{1}{T_s} \left[(\mathbf{v} - \mathbf{v}_s) \cdot \left(\mathcal{T} - \frac{1}{2} (\mathbf{E} \otimes \mathbf{P} - \mathbf{P} \otimes \mathbf{E}) - \left(\frac{1}{2} \rho |\mathbf{v}_s - \mathbf{v}|^2 + T \rho \left(\frac{\mu_{0\pm}}{T} - \frac{\mu_{\pm}}{T_s} \right) \right) \mathbf{1} \right) \nu \right]}_{=\xi_{\mathcal{V}}^{\mathcal{V}}} \\
&\quad - \underbrace{\left[\sum_{\alpha \in \mathcal{I}^{\pm} \setminus \{A_{0\pm}\}} \left(J_{\alpha,\nu} + \rho_{\alpha} (v_{\nu} - v_{\nu}) \right) \cdot \left(\frac{\mu_{\alpha} - \mu_{0\pm}}{T} - \frac{\mu_{\alpha} - \mu_{0\pm}}{T_s} \right) \right]}_{=\xi_{MT}^{\mathcal{V}}}. \tag{5.14}
\end{aligned}$$

We identify six dissipation mechanisms: tangential surface viscosity $\xi_s^{\mathcal{T}\nabla}$, tangential surface thermo-diffusion $\xi_{TD}^{\mathcal{T}}$, surface reactions ξ_s^R , heat transport normal to the surface $\xi_H^{\mathcal{V}}$, mass transport normal to the surface $\xi_{MT}^{\mathcal{V}}$, and viscosity normal to the surface $\xi_{\mathcal{V}}^{\mathcal{V}}$.

Thermodiffusion: We choose phenomenological coefficients $\kappa_s, L_{\beta}, M_{\alpha\beta}$, such that the coefficient matrix is symmetric and positive definite. We set for $\alpha \in \mathcal{I}_S \setminus \{A_0\}$

$$q_s^{\Delta} = -\frac{\kappa_s}{T_s^2} g^{\Delta\Gamma} T_s_{\parallel\Gamma} - \sum_{\beta \in \mathcal{I}_S \setminus \{A_0\}} L_{\beta} \left[g^{\Delta\Gamma} \left(\frac{\mu_{\beta}}{T_s} - \frac{\mu_0}{T_s} \right)_{\parallel\Gamma} - \frac{1}{T_s} \left(\frac{z_{\beta} e_0}{m_{\beta}} - \frac{z_0 e_0}{m_0} \right) \bar{\mathbf{E}}_{\tau}^{\Delta} \right], \tag{5.15a}$$

$$J_{s,\alpha,\tau}^{\Delta} = -\frac{L_{\alpha}}{T_s^2} g^{\Delta\Gamma} T_s_{\parallel\Gamma} - \sum_{\beta \in \mathcal{I}_S \setminus \{A_0\}} M_{\alpha\beta} \left[g^{\Delta\Gamma} \left(\frac{\mu_{\beta}}{T_s} - \frac{\mu_0}{T_s} \right)_{\parallel\Gamma} - \frac{1}{T_s} \left(\frac{z_{\beta} e_0}{m_{\beta}} - \frac{z_0 e_0}{m_0} \right) \bar{\mathbf{E}}_{\tau}^{\Delta} \right]. \tag{5.15b}$$

Surface reactions: We neglect cross effects between the different reactions and apply the nonlinear closure relations with positive phenomenological coefficients A_s^{ℓ}, R_s^{ℓ}

$$R_s^{\ell} = R_s^{\ell} \left(1 - \exp \left(\frac{A_s^{\ell}}{k_B T_s} \sum_{\alpha \in \mathcal{I}_S} \gamma_{\alpha}^{\ell} m_{\alpha} \mu_{\alpha} \right) \right). \tag{5.16}$$

Surface viscosity: Linear closure for the trace and for the deviatoric part of the surface stress tensor \mathcal{T}_s with phenomenological coefficients satisfying $\eta_b + \eta_s \geq 0$ and $\eta_s \geq 0$, yields the constitutive equation

$$\mathcal{T}_s = \eta_b \text{trace}(\mathcal{D} \mathbf{g}^{-1}) \mathbf{g}^{-1} + 2\eta_s \mathbf{g}^{-T} \mathcal{D} \mathbf{g}^{-1}. \quad (5.17)$$

This implies for the symmetric surface stress tensor the constitutive equation

$$S^{\Gamma\Delta} = \left(\rho u - T \rho \tilde{\eta} - \sum_{\alpha \in \mathcal{I}_s} \mu_\alpha \rho_\alpha \right) g^{\Delta\Gamma} + \mathcal{T}_s^{\Gamma\Delta}. \quad (5.18)$$

Heat flux normal to the surface: We choose coefficients κ_s^\pm , and obtain from linear closure

$$\left(Q_\nu + (T \rho \tilde{\eta} + \sum_{\alpha \in \mathcal{I}^\pm} \rho_\alpha \mu_\alpha) (v_\nu - v_\nu) \right)^\pm = \pm \kappa_s^\pm \left(\frac{1}{T} - \frac{1}{T} \right)^\pm. \quad (5.19)$$

Stress from the volume: We choose coefficients $\lambda_s^\pm, \eta_\Delta^\pm > 0$, for $\Delta = 1, 2$, and obtain from linear closure

$$\left(\boldsymbol{\nu} \cdot \left(\mathcal{T} - \frac{1}{2}(\mathbf{E} \otimes \mathbf{P} - \mathbf{P} \otimes \mathbf{E}) \right) \boldsymbol{\tau}_\Gamma g^{\Gamma\Delta} \right)^\pm = \pm \eta_\Delta^\pm \left(v_\tau^\Delta - v_\tau^\Delta \right)^\pm. \quad (5.20a)$$

$$\left(\boldsymbol{\nu} \cdot \left(\mathcal{T} - \frac{1}{2}(\mathbf{E} \otimes \mathbf{P} - \mathbf{P} \otimes \mathbf{E}) \right) \boldsymbol{\nu} - \left(\frac{1}{2} \rho |\mathbf{v}_s - \mathbf{v}|^2 + T_s \rho \left(\frac{\mu_{0\pm}}{T} - \frac{\mu_{0\pm}}{T_s} \right) \right)^\pm = \pm \lambda_s^\pm \rho^\pm \left(\rho (v_\nu - v_\nu) \right)^\pm. \quad (5.20b)$$

Mass transport normal to the surface: The mass transport normal to the surface can be related with adsorption, which in the context of electrothermodynamics is formally different from mass production due to chemical reactions. However, in experiments it might not always be clear how to distinguish between adsorption and surface reactions and we therefore here also apply non-linear closure similar to the chemical reactions. We neglect cross effects and choose for $\alpha \in \mathcal{I}^\pm \setminus \{A_{0\pm}\}$ coefficients β_α^\pm and $M_\alpha^\pm > 0$ to obtain for $\alpha \in \mathcal{I}^\pm \setminus \{A_{0\pm}\}$

$$D_\alpha^\pm = \left(\mu_\alpha - \mu_{0\pm} - \frac{T}{T_s} \left(\mu_\alpha - \mu_{0\pm} \right) \right)^\pm, \quad (5.21a)$$

$$\left(J_{\alpha,\nu} + \rho_\alpha (v_\nu - v_\nu) \right)^\pm = \mp M_\alpha^\pm \left(\exp \left(\frac{\beta_\alpha^\pm}{k_B T} D_\alpha^\pm \right) - \exp \left(\frac{\beta_\alpha^\pm - 1}{k_B T} D_\alpha^\pm \right) \right). \quad (5.21b)$$

5.3 Discussion of a general free energy model

The obtained constitutive equations are general, in the sense that they have been derived without making use of any particular specific material properties. They only rely on the universal balance

equations and the entropy principle. All material properties of a specific electrochemical system thus have to be incorporated into the constitutive functions of the entropy and the phenomenological coefficients. We now restrict the constitutive function for the free energy to the structure

$$\rho\psi = \hat{\rho}\psi(T, (\rho_\alpha)_{\alpha \in \mathcal{I}}) + \rho\check{\psi}^{\text{pol},P}(T, (\rho_\alpha)_{\alpha \in \mathcal{I}}, |\mathbf{P}|), \quad (5.22)$$

where the first part is independent of the electromagnetic field and the second part depends only on the absolute value of \mathbf{P} . Different free energy models can be used for the field-independent free energy contribution $\hat{\rho}\psi$, depending on the considered material. For liquid electrolytes, the model of simple mixtures of solvated ions, cf. [8, 12], appears to be appropriate. The general construction of suitable free energies and their incompressible limit is analyzed in [5]. The analysis emphasizes the importance of linear approaches with respect to the partial molar volume and illustrates the possibility to recover non-linear behaviour of the mixtures based on the non-linear reaction behaviour. As an example of a different material model, we refer to [19] modeling yttria-stabilized zirconia.

Dielectric susceptibility and Debye relaxation. Since it might appear more familiar to formulate constitutional equations in terms of \mathbf{E} instead of \mathbf{P} , we introduce a conjugate variable to \mathbf{P} that coincides with \mathbf{E} in the case of polarization equilibrium. We define

$$\mathbf{E}^{\text{Eq}} := \frac{\partial \rho\check{\psi}^{\text{pol},P}}{\partial \mathbf{P}} = -T \frac{\partial \rho\check{\eta}}{\partial \mathbf{P}}. \quad (5.23)$$

Then, we consider a change of variables by means of the Legendre transformation

$$\rho\psi^{\text{pol}} = \rho\check{\psi}^{\text{pol},P} - \mathbf{E}^{\text{Eq}} \cdot \mathbf{P}, \quad (5.24)$$

such that we have the following representation and the relations

$$\rho\psi^{\text{pol}} = \rho\check{\psi}^{\text{pol}}(T, (\rho_\alpha)_{\alpha \in \mathcal{I}}, |\mathbf{E}^{\text{Eq}}|), \quad \frac{\partial \rho\check{\psi}^{\text{pol}}}{\partial \mathbf{E}^{\text{Eq}}} = -\mathbf{P}. \quad (5.25)$$

We introduce the scalar dielectric susceptibility as

$$\chi = -\frac{1}{\varepsilon_0 |\mathbf{E}^{\text{Eq}}|} \frac{\partial}{\partial |\mathbf{E}^{\text{Eq}}|} \rho\check{\psi}^{\text{pol}}(T, (\rho_\alpha)_{\alpha \in \mathcal{I}}, |\mathbf{E}^{\text{Eq}}|), \quad (5.26)$$

such that by (5.25) implies for the vector of polarization that

$$\mathbf{P} = \chi(T, (\rho_\alpha)_{\alpha \in \mathcal{I}}, |\mathbf{E}^{\text{Eq}}|) \cdot \varepsilon_0 \mathbf{E}^{\text{Eq}}. \quad (5.27)$$

Considering the case of vanishing velocity, i.e., $\mathbf{v} = 0$, the constitutive equations (5.10) reduces to

$$\tau^P \partial_t \mathbf{P} = + \left(\varepsilon_0 \mathbf{E} - \frac{1}{\chi} \mathbf{P} \right), \quad (5.28)$$

where the relaxation constants $\tau^P > 0$ is positive. From $\text{div}(\varepsilon_0 \mathbf{E} + \mathbf{P}) = n^{\text{F}}$, we conclude that for the divergence of the constitutive equation (5.28) it holds

$$\tau^P \partial_t \text{div}(\mathbf{P}) = n^{\text{F}} - \left(1 + \frac{1}{\chi} \right) \text{div}(\mathbf{P}). \quad (5.29)$$

We conclude that if $n^{\text{F}} = 0$ in equation (5.29), then $\text{div}(\mathbf{P})$ vanishes for $t \rightarrow \infty$, what is compatible with stable polarization relaxation. We remark, that the stability of relaxation does not depend on the applied change of variables.

Pressure, surface tension and stress tensor. In the context of electro-thermodynamics, proper definition of pressure is not obvious. We define here pressure based on only these contributions that are also present in the absence of electromagnetic fields. By the Gibbs–Duhem relation known from classical thermodynamics and its counterpart on the surface, cf. [7, 15], we define pressure and surface tension as

$$\hat{p} = -\rho\hat{\psi} + \sum_{\alpha \in \mathcal{I}^\pm} \rho_\alpha \hat{\mu}_\alpha, \quad \gamma = \rho\psi - \sum_{\alpha \in \mathcal{I}_S} \rho_\alpha \mu_\alpha, \quad (5.30)$$

where the splitting of the free energy in (5.22) implies a similar splitting of the chemical potentials. The Legendre transformation (5.3) implies

$$\mu_\alpha = \frac{\partial \rho\hat{\psi}}{\partial \rho_\alpha} + \frac{\partial \rho\check{\psi}^{\text{pol}}}{\partial \rho_\alpha} = -T \frac{\partial \rho\tilde{\eta}}{\partial \rho_\alpha}, \quad (5.31a)$$

$$\mu_\alpha = \frac{\partial \rho\hat{\psi}}{\partial \rho_\alpha} = -T \frac{\partial \rho\tilde{\eta}}{\partial \rho_\alpha} \quad (5.31b)$$

With the above definitions of pressure and surface tension, we can rewrite the stress tensor in the volume in (5.12) and on the surface in (5.18) as

$$\Sigma - \sigma^{\text{EM}} = \mathcal{T} - \left(\hat{p} - \rho\check{\psi}^{\text{pol}} + \sum_{\alpha \in \mathcal{I}^\pm} \rho_\alpha \frac{\partial \rho\check{\psi}^{\text{pol}}}{\partial \rho_\alpha} \right) \mathbf{1} + \frac{1}{2}(\mathbf{E} \otimes \mathbf{P} + \mathbf{P} \otimes \mathbf{E}) - \mathbf{P} \cdot (\mathbf{E} - \mathbf{E}^{\text{Eq}}) \mathbf{1}, \quad (5.32a)$$

$$S^{\Gamma\Delta} = \mathcal{T}_s^{\Gamma\Delta} + \gamma_s g^{\Gamma\Delta}. \quad (5.32b)$$

Using the scalar susceptibility χ according to (5.26) and assuming polarization relaxation equilibrium, i.e. $\mathbf{E}^{\text{Eq}} = \mathbf{E}$, such that $\mathbf{P} = \chi\varepsilon_0\mathbf{E}$ according to (5.27), we infer with the Maxwell stress tensor according to (3.25) that

$$\Sigma = -\hat{p}\mathbf{1} + \mathcal{T} + \sigma^{\text{EM}} + \chi\varepsilon_0\mathbf{E} \otimes \mathbf{E} + \left(\rho\check{\psi}^{\text{pol}} - \sum_{\alpha \in \mathcal{I}^\pm} \rho_\alpha \frac{\partial \rho\check{\psi}^{\text{pol}}}{\partial \rho_\alpha} \right) \mathbf{1}. \quad (5.33)$$

Due to the structural similarity to (5.30), one might refer to the last bracket in (5.33) as polarization pressure. Nevertheless, we prefer to keep this term separate from the pressure contribution \hat{p} to the stress tensor and relate the the last terms in (5.30) to forces in the momentum balance. In the particular case of constant χ , we check $\rho\check{\psi}^{\text{pol}} = -\frac{1}{2}\chi\varepsilon_0|\mathbf{E}|^2$ such that the stress tensor further simplifies to $\Sigma = -\hat{p}\mathbf{1} + \mathcal{T} + (1 + \chi)\sigma^{\text{EM}}$.

Application to momentum balance. We again assume $\mathbf{E}^{\text{Eq}} = \mathbf{E}$ and $\mathbf{P} = \chi\varepsilon_0\mathbf{E}$. The divergence of the Maxwell stress tensor σ^{EM} equals in the quasi-electrostatic limit the Lorenz force $n^e\mathbf{E}$ and it seems appropriate to treat also the divergence of the last two terms in (5.33) as forces in the momentum balance. Whenever χ is independent of the concentrations, i.e. independent of all ρ_α for $\alpha \in \mathcal{I}$, we apply $\nabla \rho\check{\psi}^{\text{pol}} = -(\nabla \mathbf{E}^{\text{Eq}}) \mathbf{P} = -\chi(\nabla \mathbf{E}) \varepsilon_0\mathbf{E}$, to conclude for the divergence of the stress tensor in the momentum balance

$$\text{if } \chi \text{ independent of all } \rho_\alpha : \quad \text{div}(\Sigma) = -\nabla\hat{p} + \text{div}(\mathcal{T}) + \underbrace{\text{div}((1 + \chi)\varepsilon_0\mathbf{E})}_{=n^F} \mathbf{E}. \quad (5.34)$$

Due to its similarity, the term $n^F \mathbf{E}$ is also referred to as Lorentz force. On the other hand, if $\rho \check{\psi}^{\text{pol}}$ is a homogeneous function of degree one with respect to all ρ_α for $\alpha \in \mathcal{I}$, then χ is a homogeneous function as well and the terms in the bracket in (5.33) cancel. We conclude

$$\text{if } \rho \check{\psi}^{\text{pol}} \text{ homogeneous function of } \rho_\alpha : \quad \text{div}(\boldsymbol{\Sigma}) = -\nabla \hat{p} + \text{div}(\boldsymbol{\mathcal{T}}) + n^F \mathbf{E} + \chi(\nabla \mathbf{E}) \varepsilon_0 \mathbf{E}. \quad (5.35)$$

In addition to the Lorentz force, the last term in (5.35) is referred to as Kelvin polarization force. In the momentum balance on the surface, we have

$$\left(\sigma_s^{i\Delta} \right)_{\parallel \Delta} = \gamma_{\parallel \Delta} g_s^{\Gamma \Delta} \tau_{\Gamma}^i + 2\gamma k_M \nu^i. \quad (5.36)$$

6 Constitutive Equations for the quasi-magnetostatic limit

The construction of constitutive relations for the quasi-magnetostatic limit follows largely along the same lines as described in the previous section. The entropy principle is now based on constitutive functions of the entropy density in the form

$$\rho \eta = \tilde{\rho} \tilde{\eta}(\rho u, (\rho_\alpha)_{\alpha \in \mathcal{I}^\pm}, \mathbf{B}), \quad \rho \eta = \tilde{\rho} \tilde{\eta}(\rho u, (\rho_\alpha)_{\alpha \in \mathcal{I}_S}). \quad (6.1a)$$

The (absolute) temperature T, T_s and the chemical potentials μ_α, μ_α are defined in analogous way as in (5.2) and we introduce the free energy in analogous way as in (5.3). More specific, we restrict the constitutive function for the free energy to the structure

$$\rho \psi = \hat{\rho} \hat{\psi}(T, (n_\alpha)_{\alpha \in \mathcal{I}}) + \rho \psi^{\text{mag}}(T, (n_\alpha)_{\alpha \in \mathcal{I}}, |\mathbf{B}|), \quad (6.2)$$

such that the splitting of the free energy implies similar splitting of the chemical potentials. As in (5.30), we define

$$\hat{p} = -\rho \hat{\psi} + \sum_{\alpha \in \mathcal{I}^\pm} \rho_\alpha \hat{\mu}_\alpha, \quad \gamma = \rho \psi - \sum_{\alpha \in \mathcal{I}_S} \rho_\alpha \mu_\alpha. \quad (6.3)$$

6.1 Constitutive Relations for the Bulk

Taking the same entropy flux as above, the entropy production mostly looks the same as in (5.7) and we identify again five dissipative mechanism, where only polarization is now replaced by magnetization. We proceed in the same way as in Sect. 5 and apply closure relations to each dissipative mechanism. For the reactions, there is no change to (5.9).

Thermodiffusion: Compared to (5.8a), there is only a difference in the driving force of the migration term. We choose coefficients $\kappa, L_\beta, M_{\alpha\beta}$ such that the coefficient matrix is symmetric and positive definite. and set

$$\mathbf{Q} = -\frac{\kappa}{T^2} \nabla T - \sum_{\beta \in \mathcal{I}^\pm \setminus \{A_{0\pm}\}} L_\beta \left(\nabla \left(\frac{\mu_\beta}{T} - \frac{\mu_{0\pm}}{T} \right) - \frac{1}{T} \left(\frac{z_\beta e_0}{m_\beta} - \frac{z_{0\pm} e_0}{m_{0\pm}} \right) (\mathbf{v} \times \mathbf{B}) \right), \quad (6.4a)$$

$$\mathbf{J}_\alpha = -\frac{L_\alpha}{T^2} \nabla T - \sum_{\beta \in \mathcal{I}^\pm \setminus \{A_{0\pm}\}} M_{\alpha\beta} \left(\nabla \left(\frac{\mu_\beta}{T} - \frac{\mu_{0\pm}}{T} \right) - \frac{1}{T} \left(\frac{z_\beta e_0}{m_\beta} - \frac{z_{0\pm} e_0}{m_{0\pm}} \right) (\mathbf{v} \times \mathbf{B}) \right). \quad (6.4b)$$

Magnetization: The entropy production due to magnetization is

$$\xi_M = + \left(\frac{\partial \rho \tilde{\eta}}{\partial \mathbf{B}} - \frac{1}{T} \mathbf{M} \right) \cdot \left(\partial_t \mathbf{B} + (\mathbf{v} \cdot \nabla) \mathbf{B} - \frac{1}{2} (\nabla \mathbf{v} - \nabla \mathbf{v}^T) \mathbf{B} \right). \quad (6.5)$$

We choose a linear closure relation with the relaxation time $\tau^M > 0$ of polarization to obtain

$$\tau^M \frac{1}{\mu_0} (\partial_t \mathbf{B} + (\nabla \mathbf{B}) \mathbf{v} - \frac{1}{2} (\nabla \mathbf{v} - \nabla \mathbf{v}^T) \mathbf{B}) = T \frac{\partial \rho \tilde{\eta}}{\partial \mathbf{B}} - \mathbf{M}. \quad (6.6)$$

We introduce the conjugate variable \mathbf{M}^{Eq} and the scalar magnetic susceptibility χ_M as

$$\mathbf{M}^{\text{Eq}} := - \frac{\partial \rho \psi}{\partial \mathbf{B}} = T \frac{\partial \rho \tilde{\eta}}{\partial \mathbf{B}}, \quad \frac{\chi_M}{1 + \chi_M} = - \frac{\mu_0}{|\mathbf{B}|} \frac{\partial}{\partial |\mathbf{B}|} \rho \psi^{\text{mag}}(T, (n_\alpha)_{\alpha \in \mathcal{I}}, |\mathbf{B}|), \quad (6.7)$$

where $\chi_M = \chi_M(T, (n_\alpha)_{\alpha \in \mathcal{I}}, |\mathbf{B}|)$ and we have

$$\mathbf{M}^{\text{Eq}} = \frac{\chi_M}{1 + \chi_M} \cdot \frac{1}{\mu_0} \mathbf{B}. \quad (6.8)$$

In magnetization equilibrium (6.5) implies $\mathbf{M}^{\text{Eq}} = \mathbf{M}$. When we consider the case of vanishing velocity, i.e., $\mathbf{v} = 0$ the constitutive equation (6.6) simplifies to

$$\tau^M \frac{1}{\mu_0} \partial_t \mathbf{B} = - \left(- \frac{\chi_M}{1 + \chi_M} \frac{1}{\mu_0} \mathbf{B} + \mathbf{M} \right), \quad (6.9)$$

From $\text{curl}(\frac{1}{\mu_0} \mathbf{B} - \mathbf{M}) = \mathbf{J}^{\text{F}}$, we conclude for the curl of (6.9) that

$$\tau^B \partial_t \text{curl}(\mathbf{B}) = \mathbf{J}^{\text{F}} - \left(- \frac{\chi_M}{1 + \chi_M} + 1 \right) \text{curl}(\mathbf{B}). \quad (6.10)$$

We conclude stable magnetization relaxation for $\mathbf{J}^{\text{F}} = 0$ and $\chi_M > -1$, i.e. $\text{curl}(\mathbf{B})$ vanishes for $t \rightarrow \infty$. While $\chi_M > 0$ represents paramagnetic material behaviour, $\chi_M < 0$ characterizes diamagnetic materials. The limit $\chi_M = -1$ represents superconducting materials.

Viscosity: Taking for the viscous stress tensor the same approach as in (5.11), i.e. $\mathcal{T} = \eta_b \text{div}(\mathbf{v}) \mathbf{1} + \eta_s (\nabla \mathbf{v} + (\nabla \mathbf{v})^T)$, yields for the symmetric total stress tensor Σ in the quasi-magnetostatic limit the constitutive equation

$$\Sigma - \sigma^{\text{EM}} = \mathcal{T} + \left(\rho u - T \rho \tilde{\eta} + \mathbf{M} \cdot \mathbf{B} - \sum_{\alpha \in \mathcal{I}^\pm} \rho_\alpha \mu_\alpha \right) \mathbf{1} - \frac{1}{2} (\mathbf{M} \otimes \mathbf{B} + \mathbf{B} \otimes \mathbf{M}). \quad (6.11)$$

With the definition of pressure according to (6.3), the free energy as in (6.2) with the scalar magnetic susceptibility according to (6.7), and assuming magnetization relaxation equilibrium, i.e. $\mathbf{M}^{\text{Eq}} = -\mathbf{M}$, we obtain

$$\Sigma = -\hat{p} \mathbf{1} + \mathcal{T} + \sigma^{\text{EM}} - \frac{\chi_M}{1 + \chi_M} \frac{1}{\mu_0} \mathbf{B} \otimes \mathbf{B} + \left(\rho \psi^{\text{mag}} - \sum_{\alpha \in \mathcal{I}^\pm} \rho_\alpha \frac{\partial \rho \psi^{\text{mag}}}{\partial \rho_\alpha} + \frac{\chi_M}{1 + \chi_M} \frac{1}{\mu_0} |\mathbf{B}|^2 \right) \mathbf{1}, \quad (6.12)$$

where in the case of constant χ_M , we have $\rho \psi^{\text{mag}} = - \frac{\chi_M}{1 + \chi_M} \frac{1}{2\mu_0} |\mathbf{B}|^2$ and the stress tensor further simplifies to $\Sigma = -\hat{p} \mathbf{1} + \mathcal{T} + \frac{1}{1 + \chi_M} \sigma^{\text{EM}}$.

The divergence of the Maxwell stress tensor σ^{EM} equals in the quasi-magnetostatic limit the Lorenz force $(n^e \mathbf{v} + \mathbf{J}^e) \times \mathbf{B}$ and it seems appropriate to treat also the divergence of the last two terms in (6.12) as forces in the momentum balance.

6.2 Constitutive Relations for the Surface

We use the definitions of \mathcal{T}_s and \mathcal{D}_s as in (5.13) to derive the surface entropy production in analogously way as before. For the surface reactions there is no change to (5.16) and for the viscous stress tensor on the surface there is no change to (5.17).

Thermodiffusion: With the same choice of the symmetric and positive definite coefficient matrix, we set as in (5.15) for $\alpha \in \mathcal{I}_S \setminus \{A_0\}$

$$q_s^\Delta = -\frac{\kappa_s}{T_s^2} g^{\Delta\Gamma} T_s \parallel_\Gamma - \sum_{\beta \in \mathcal{I}_S \setminus \{A_0\}} L_s^\beta \left[g^{\Delta\Gamma} \left(\frac{\mu_\beta}{T_s} - \frac{\mu_0}{T_s} \right) \parallel_\Gamma - \frac{1}{T_s} \left(\frac{z_\beta e_0}{m_\beta} - \frac{z_0 e_0}{m_0} \right) (\mathbf{v}_s \times \bar{\mathbf{B}})^\Delta_\tau \right], \quad (6.13a)$$

$$J_{s,\alpha,\tau}^\Delta = -\frac{L_\alpha}{T_s^2} g^{\Delta\Gamma} T_s \parallel_\Gamma - \sum_{\beta \in \mathcal{I}_S \setminus \{A_0\}} M_{s,\alpha\beta} \left[g^{\Delta\Gamma} \left(\frac{\mu_\beta}{T_s} - \frac{\mu_0}{T_s} \right) \parallel_\Gamma - \frac{1}{T_s} \left(\frac{z_\beta e_0}{m_\beta} - \frac{z_0 e_0}{m_0} \right) (\mathbf{v}_s \times \bar{\mathbf{B}})^\Delta_\tau \right]. \quad (6.13b)$$

Stress coming from the volume: We choose coefficients $\lambda_s^\pm, \eta_\Delta^\pm > 0$, for $\Delta = 1, 2$, and obtain from linear closure

$$\left(\boldsymbol{\nu} \cdot \left(\mathcal{T} + \frac{1}{2}(\mathbf{M} \otimes \mathbf{B} - \mathbf{B} \otimes \mathbf{M}) \right) \boldsymbol{\tau}_\Gamma g^{\Gamma\Delta} \right)^\pm = \pm \eta_\Delta^\pm \left(v_\tau^\Delta - v_{s,\tau}^\Delta \right)^\pm, \quad (6.14a)$$

$$\begin{aligned} \left(\boldsymbol{\nu} \cdot \left(\mathcal{T} + \frac{1}{2}(\mathbf{M} \otimes \mathbf{B} - \mathbf{B} \otimes \mathbf{M}) \right) \boldsymbol{\nu} - \left(\frac{1}{2} \rho |v_s - \mathbf{v}|^2 + T_s \rho \left(\frac{\mu_{0\pm}}{T} - \frac{\mu_s}{T_s} \right) \right) \right)^\pm \\ = \pm \lambda_s^\pm \rho^\pm \left(\rho (v_\nu - v_{s,\nu}) \right)^\pm. \end{aligned} \quad (6.14b)$$

7 Summary and discussion

By asymptotic considerations, we have motivated the formulation of two distinct Galilean limit systems of the Maxwell equations. Both Galileo limits are well known for volume domains and have here been transferred to surfaces. Due to its transformation properties, each one of these limit systems can easily be coupled in a consistent manner to standard non-relativistic balance equations of matter that are well suited for most engineering applications. Then, constitutive equations to close the coupled system can be obtained from an entropy principle.

Comparison to results of [9]. Considering first the quasi-electrostatic limit, the same results as here in Sect. 5, in principle can also be obtained by [9], where full the Maxwell equations are employed and the quasi-electrostatic limit then can be taken after the application of the entropy principle. However, this procedure is less straightforward, because in [9] the inner energy density of the coupled system is redefined in order to obtain the entropy production related to magnetization as a binary product satisfying a Galilei symmetry principle. Such a modification of the inner energy as $\rho u + \mathcal{M} \cdot \mathbf{B}$ seems admissible because in coupled electro-thermodynamics it is not a-priori evident what is the correct

definition of inner energy. The non-dimensionalization of Sect. 3.3 reveals that this modification made to the inner energy is asymptotically small in the quasi-electrostatic limit and can therefore be neglected.

An alternative application of the entropy principle based on \mathcal{E} as independent variable is discussed in [9]. It relies on a different definition of the inner energy as $\rho u - \mathcal{E} \cdot \mathbf{P}$ and therefore it is fundamentally different from the change of variables employed here in Sect. 5.3. The term $\mathcal{E} \cdot \mathbf{P}$ is not asymptotically small compared to ρu in the quasi-electrostatic limit, and thus implies a non-negligible difference in the definition of temperature. Moreover, the application of a linear closure relation then yields an unstable relaxation of polarization. In contrast, the change of variables applied here in Sect. 5.3 and in the same way also in [13], changing the variables from \mathbf{P} to \mathbf{E}^{Eq} , does not alter the stability of polarization relaxation and in equilibrium we have $\mathbf{E}^{\text{Eq}} = \mathbf{E}$.

In addition, the entropy principle in [9] also covers magnetization. We omitted magnetization here in Sect. 5, because in the quasi-electrostatic limit the corresponding contributions to the entropy production are in the asymptotic order of the terms that we neglected in the balance equations. Without a constitutive equation relating \mathbf{B} and \mathcal{M} , we are in general not able to evaluate the electric current \mathbf{j}^{e} , although in many experiments this is the observable quantity of pivotal importance. So either an additional constitutive law has to be obtained from a different source, or we have to apply an additional asymptotic limit such as the thin double layer limit where the contribution to \mathbf{j}^{e} due to \mathcal{M} vanishes. Relaxation of magnetization is not discussed in [9]. We note, that an analogous approach as performed here in Sect. 6, but applied to the main approach of [9] based on the variables $(\mathbf{P}, \mathcal{M})$, would imply blow up of $\text{curl}(\mathcal{M})$ for diamagnetic material.

In the quasi-magnetostatic limit, we assumed in Sect. 6 the entropy density to depend on the independent variable \mathcal{E} . This is different than the main approach of [9], but compatible with the alternative approach discussed there and with [15]. Within the quasi-magnetostatic limit, the definition of the inner energy as $\rho u - \mathcal{E} \cdot \mathbf{P}$ is a negligible modification, whereas $\mathcal{M} \cdot \mathbf{B}$ is not asymptotically small. Accordingly, we observed in Sect. 6 stable relaxation of magnetization, whereas the approach based on the variable \mathcal{M} would lead to unstable relaxation for diamagnetic material.

Each of the modifications of the inner energy in [9] implies according changes to the stress tensor when it is expressed in terms of free energy. Non-constant susceptibility requires careful treatment of the momentum balance, cf. [13].

Conclusions for coupling with general Maxwell equations. Coupling the full Maxwell equations to the non-relativistic balance equations of matter, appears to be a more general approach than the one presented here. For this general case, two alternative formulations of the entropy principle have been analyzed in [9], one based on the variables $(\mathbf{P}, \mathcal{M})$, the other one based on the variables $(\mathcal{E}, \mathbf{B})$. While the $(\mathbf{P}, \mathcal{M})$ -variant allows to reach the quasi-electrostatic Galileo limit where only \mathbf{P} remains as a variable, the $(\mathcal{E}, \mathbf{B})$ -variant allows to reach the quasi-magnetostatic Galileo limit with only \mathbf{B} as remaining variable. Neither of the two variants is capable to cover both limit cases equally well, as for the $(\mathbf{P}, \mathcal{M})$ -variant magnetization relaxation is unstable for diamagnetic material, whereas for the $(\mathcal{E}, \mathbf{B})$ -variant polarization relaxation is unstable. However, this should not be considered a source of inconsistency for the limit cases, as the two Galilei limits do not have any relevant overlap. We remark that building the entropy principle on (\mathbf{P}, \mathbf{B}) as independent variables does not provide a remedy for the general case, since \mathbf{P} and \mathbf{B} do not form an antisymmetric four-tensor in the four-dimensional formulation of the Maxwell equations. Therefore, we conclude that *if* electric and magnetic effects both are relevant in the application, *then* one is well advised to consider in addition to the general Maxwell equations also a relativistic description of the mixture of matter. This leaves it as an open question, how to find appropriate models for e.g. liquid metal batteries or magneto-hydrodynamic forces in the

electrolyte transport of the Hall-Heroult process.

Electrochemical model in polarization equilibrium. We summarize here the complete system of model equations for electrochemical applications under the simplifying assumption of fast polarization relaxation. An important feature of electrochemical systems is the formation of double layers at the contact of different materials. The double layer is characterized by a typical width in the range of nanometers wherein the electric potential may vary in the order of one Volt. The magnetic field strength is assumed to be below a guideline value for electromagnetic fields in electrical household appliances. These reference values

$$B^{\text{ref}} = 10^{-3} \frac{\text{Vs}}{\text{m}^2}, \quad E^{\text{ref}} = 10^9 \frac{\text{V}}{\text{m}}, \quad c_0 \approx 3 \cdot 10^8 \frac{\text{m}}{\text{s}}, \quad (7.1)$$

imply for the dimensionless quantity

$$\beta^2 \approx 3 \cdot 10^{-4} \ll 1. \quad (7.2)$$

The smallness of β^2 suggests the use of the quasi-electrostatic limit, where (3.23b) implies the existence of an *electrostatic potential* φ , such that

$$\mathbf{E} = -\nabla\varphi, \quad [[\varphi]] = \text{const. on } S, \quad (7.3)$$

where the constant is frequently chosen as zero.

For each volume domain Ω^\pm , we use index sets \mathcal{I}^\pm for the constituents of the mixture. The constitutive equations in the volume are build on a free energy density of the structure

$$\rho\psi = \hat{\rho}\psi(T, (\rho_\alpha)_{\alpha \in \mathcal{I}}) + \rho\psi^{\text{pol}}(T, (\rho_\alpha)_{\alpha \in \mathcal{I}}, |\nabla\varphi|), \quad (7.4)$$

The chemical potentials for $\alpha \in \mathcal{I}^\pm$, pressure and the inner energy are given in terms of the free energy as

$$\mu_\alpha = \frac{\partial}{\partial \rho_\alpha} \rho\psi, \quad p = -\rho\hat{\psi} + \sum_{\alpha \in \mathcal{I}^\pm} \rho_\alpha \hat{\mu}_\alpha, \quad \rho u = \left(T^2 \frac{\partial}{\partial T} \frac{\rho\psi}{T} \right). \quad (7.5)$$

The dielectric susceptibility is defined as

$$\chi = -\frac{1}{\varepsilon_0 |\nabla\varphi|} \frac{\partial}{\partial |\nabla\varphi|} \rho\psi^{\text{pol}}(T, (\rho_\alpha)_{\alpha \in \mathcal{I}}, |\nabla\varphi|). \quad (7.6)$$

Since polarization relaxation in liquid electrolytes is typically fast with a time constant in the range of 10^{-8} s, cf. [6], we can assume that polarization relaxation is in quasi-equilibrium, i.e., $\mathbf{P} = -\chi\varepsilon_0 \nabla\varphi$. In the following we distinguish two cases

$$\chi \text{ is } \begin{cases} \text{independent of } \rho_\alpha, & \text{indicated as } (*), \\ \text{homogeneous of degree 1 in } \rho_\alpha, & \text{indicated as } (**). \end{cases} \quad (7.7)$$

In each volume domain, we chose a constituent $A_{0,\pm} \in \mathcal{I}^\pm$. Then, the balance equations are

$$-\operatorname{div}((1 + \chi)\varepsilon_0 \nabla \varphi) = n^F, \quad (7.8a)$$

$$\partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha \mathbf{v} + \mathbf{J}_\alpha) = m_\alpha \sum_k \gamma_\alpha^k R^k \quad \text{for } \alpha \in \mathcal{I}^\pm \setminus \{A_{0,\pm}\}, \quad (7.8b)$$

$$\partial_t \rho + \operatorname{div}(\rho \mathbf{v}) = 0, \quad (7.8c)$$

$$\partial_t(\rho \mathbf{v}) + \operatorname{div}(\rho \mathbf{v} \otimes \mathbf{v} - \mathcal{T}) + \nabla p = \rho \mathbf{f} - n^F \nabla \varphi + \begin{cases} 0, & (*) \\ (D^2 \varphi) \chi \varepsilon_0 \nabla \varphi, & (**), \end{cases} \quad (7.8d)$$

$$\begin{aligned} \partial_t(\rho u) + \operatorname{div}(\rho u \mathbf{v} + \mathbf{Q}) &= -\mathbf{J}^F \cdot \nabla \varphi + \mathcal{T} : \nabla \mathbf{v} - p \operatorname{div}(\mathbf{v}) \\ &+ (\partial_t(\chi \varepsilon_0 \nabla \varphi) + (\mathbf{v} \cdot \nabla)(\chi \varepsilon_0 \nabla \varphi)) \cdot \nabla \varphi \\ &+ \operatorname{div}(\mathbf{v}) \begin{cases} \chi \varepsilon_0 |\nabla \varphi|^2 - \rho \psi^{\text{pol}}, & (*) \\ \chi \varepsilon_0 |\nabla \varphi|^2, & (**). \end{cases} \end{aligned} \quad (7.8e)$$

The constitutive equations in the volume are

$$\mathbf{Q} = -\frac{\kappa}{T^2} \nabla T - \sum_{\beta \in \mathcal{I}^\pm \setminus \{A_{0,\pm}\}} L_\beta \left(\nabla \left(\frac{\mu_\beta}{T} - \frac{\mu_{0,\pm}}{T} \right) + \frac{e_0}{T} \left(\frac{z_\beta}{m_\beta} - \frac{z_{0,\pm}}{m_{0,\pm}} \right) \nabla \varphi \right), \quad (7.9a)$$

$$\mathbf{J}_\alpha = -\frac{L_\alpha}{T^2} \nabla T - \sum_{\beta \in \mathcal{I}^\pm \setminus \{A_{0,\pm}\}} M_{\alpha\beta} \left(\nabla \left(\frac{\mu_\beta}{T} - \frac{\mu_{0,\pm}}{T} \right) + \frac{e_0}{T} \left(\frac{z_\beta}{m_\beta} - \frac{z_{0,\pm}}{m_{0,\pm}} \right) \nabla \varphi \right), \quad (7.9b)$$

$$\mathcal{T} = \eta_b \operatorname{div}(\mathbf{v}) \mathbf{1} + \eta_s \cdot (\nabla \mathbf{v} + (\nabla \mathbf{v})^T), \quad (7.9c)$$

$$R^k = R_0^k \cdot \left(1 - \exp \left(\frac{A^k}{k_B T} \sum_{\alpha \in \mathcal{I}^\pm} \gamma_\alpha^k m_\alpha \mu_\alpha \right) \right). \quad (7.9d)$$

On the surface with the index set \mathcal{I}_S for the constituents, the free energy density does not depend on the electric field. The chemical potentials for $\alpha \in \mathcal{I}_S$, surface tension and the inner energy are given in terms of the free energy as

$$\rho_{s s} \psi = \rho_{s s} \hat{\psi}(T, (\rho_\alpha)_{\alpha \in \mathcal{I}_S}), \quad \mu_{s s} = \frac{\partial}{\partial \rho_{s s}} \rho_{s s} \hat{\psi}, \quad \gamma_{s s} = \rho_{s s} \psi - \sum_{\alpha \in \mathcal{I}_S} \rho_{s s} \mu_\alpha, \quad \rho_{s s} u = \left(T_{s s}^2 \frac{\partial}{\partial T_{s s}} \frac{\rho_{s s} \hat{\psi}}{T_{s s}} \right). \quad (7.10)$$

We chose a constituent $A_0 \in \mathcal{I}_S$ and let $\alpha \in \mathcal{I}_S \setminus \{A_0\}$. Then, the surface balance equations are

$$-\varepsilon_0 \llbracket (1 + \chi) \nabla \varphi \cdot \boldsymbol{\nu} \rrbracket = n_s^F, \quad (7.11a)$$

$$\begin{aligned} \partial_{t,\nu} \rho_\alpha + \left(\rho_\alpha v_{s\tau}^\Delta + J_{s\alpha,\tau}^\Delta \right) \llbracket \Delta \\ - 2k_M v_{s\nu} \rho_\alpha = -\llbracket \rho_\alpha (v_\nu - v_\nu) + \mathbf{J}_\alpha \cdot \boldsymbol{\nu} \rrbracket + m_\alpha \sum_\ell \gamma_\alpha^\ell R_s^\ell, \end{aligned} \quad (7.11b)$$

$$\partial_{t,\nu} \rho + \left(\rho v_{s\tau}^\Delta \right) \llbracket \Delta - 2k_M v_{s\nu} \rho = -\llbracket \rho (v_\nu - v_\nu) \rrbracket. \quad (7.11c)$$

$$\begin{aligned}
\partial_{t,\nu}(\rho v^i) + \left(\rho v^i v_{s\tau}^\Delta - \mathcal{T}_s^{\Gamma\Delta} \tau_\Gamma^i \right)_{\parallel\Delta} \\
- 2k_M v_\nu \rho v^i = -[\rho v^i (v_\nu - v_\nu) + p v^i - (\mathcal{T} + (1 + \chi)\boldsymbol{\sigma}^{\text{EM}}) \cdot \boldsymbol{\nu}] \\
+ 2k_M \gamma \nu^i + \gamma_{\parallel\Delta} g^{\Gamma\Delta} \tau_\Gamma^i + \rho f^i \\
+ \left[\frac{1}{2} \chi \varepsilon_0 |\nabla \varphi|^2 \nu^i \right] + \begin{cases} [\rho \psi^{\text{pol}} \nu^i], & (*), \\ 0, & (**), \end{cases}
\end{aligned} \tag{7.11d}$$

$$\begin{aligned}
\partial_{t,\nu}(\rho u) + \left(\rho u v_{s\tau}^\Delta + q^\Delta \right)_{\parallel\Delta} \\
- 2k_M v_\nu \rho u = -\mathbf{J}_s^{\text{F}} \cdot \bar{\nabla} \varphi + (\mathcal{T}_s^{\Gamma\Delta} + \gamma g^{\Gamma\Delta}) \tau_\Gamma^i v_{s\tau}^i \\
- \left[\left(\rho u + \frac{1}{2} \rho |\mathbf{v} - \mathbf{v}_s|^2 \right) (v_\nu - v_\nu) + \mathbf{Q} \cdot \boldsymbol{\nu} \right] \\
+ [(\mathbf{v} - \mathbf{v}_s) \cdot (-p \mathbf{1} + \mathcal{T}) \cdot \boldsymbol{\nu}] + \begin{cases} [(\mathbf{v} - \mathbf{v}_s)_\nu \rho \psi^{\text{pol}}], & (*), \\ 0, & (**), \end{cases}
\end{aligned} \tag{7.11e}$$

The constitutive equations are with $\alpha \in \mathcal{I}^\pm \setminus \{A_{0\pm}\}$

$$q_\tau^\Delta = -\frac{\kappa}{T_s^2} g^{\Delta\Gamma} T_s \parallel_\Gamma - \sum_{\beta \in \mathcal{I}_S \setminus \{A_0\}} L_\beta \left[g^{\Delta\Gamma} \left(\frac{\mu_\beta}{T_s} - \frac{\mu_0}{T_s} \right) \parallel_\Gamma + \frac{e_0}{T_s} \left(\frac{z_\beta}{m_\beta} - \frac{z_0}{m_0} \right) \bar{\nabla} \varphi_\tau^\Delta \right], \tag{7.12a}$$

$$J_{s\alpha,\tau}^\Delta = -\frac{L_\alpha}{T_s^2} g^{\Delta\Gamma} T_s \parallel_\Gamma - \sum_{\beta \in \mathcal{I}_S \setminus \{A_0\}} M_{\alpha\beta} \left[g^{\Delta\Gamma} \left(\frac{\mu_\beta}{T_s} - \frac{\mu_0}{T_s} \right) \parallel_\Gamma + \frac{e_0}{T_s} \left(\frac{z_\beta}{m_\beta} - \frac{z_0}{m_0} \right) \bar{\nabla} \varphi_\tau^\Delta \right]. \tag{7.12b}$$

$$\mathcal{T}_s^{\Delta\Gamma} = \eta_b \mathcal{D}_{s\Lambda\Sigma} g^{\Lambda\Sigma} \mathbf{g}^{\Delta\Gamma} + 2\eta_s g^{\Lambda\Delta} \mathcal{D}_{s\Lambda\Sigma} g^{\Sigma\Gamma}, \tag{7.12c}$$

$$\text{with } \mathcal{D}_{s\Delta\Gamma} = \frac{1}{2} (g_{\Gamma\Lambda} v_{s\tau}^\Delta + g_{\Delta\Lambda} v_{s\tau}^\Delta) - b_{\Gamma\Delta} v_\nu, \tag{7.12d}$$

$$R_s^\ell = R_s^\ell \cdot \left(\exp \left(-\frac{\beta^\ell}{k_B T_s} D^\ell \right) - \exp \left(\frac{1 - \beta^\ell}{k_B T_s} D^\ell \right) \right), \tag{7.12e}$$

$$\text{with } D_s^\ell = A_s^\ell \sum_{\alpha \in \mathcal{I}_S} \gamma_\alpha^\ell m_\alpha \mu_\alpha. \tag{7.12f}$$

Moreover, there are the boundary conditions

$$\left(J_{\alpha,\nu} + \rho_\alpha (v_\nu - v_\nu) \right)^\pm = \mp M_s^\pm \left(\exp \left(\frac{\beta_\alpha^\pm}{k_B T} D_\alpha^\pm \right) - \exp \left(\frac{\beta_\alpha^\pm - 1}{k_B T} D_\alpha^\pm \right) \right), \tag{7.13a}$$

$$\text{with } D_\alpha^\pm = \left(\mu_\alpha - \mu_{0\pm} - \frac{T}{T_s} \left(\mu_\alpha - \mu_{0\pm} \right) \right)^\pm, \tag{7.13b}$$

$$\pm \eta_\Delta^\pm \left(v_\tau^\Delta - v_{s\tau}^\Delta \right)^\pm = (g^{\Gamma\Delta} \boldsymbol{\tau}_\Gamma \cdot \boldsymbol{\mathcal{T}} \boldsymbol{\nu})^\pm, \tag{7.13c}$$

$$\pm \lambda_s^\pm \rho^\pm \left(\rho (v_\nu - v_\nu) \right)^\pm = \left(\boldsymbol{\nu} \cdot \boldsymbol{\mathcal{T}} \boldsymbol{\nu} - \frac{1}{2} \rho |\boldsymbol{v}_s - \boldsymbol{v}|^2 - T_s \rho \left(\frac{\mu_{0\pm}}{T} - \frac{\mu_{0\pm}}{T_s} \right) \right)^\pm, \quad (7.13d)$$

$$\begin{aligned} \pm k_s^\pm \left(\frac{1}{T} - \frac{1}{T_s} \right)^\pm &= (Q_\nu + (\rho u + p) (v_\nu - v_\nu))^\pm & (7.13e) \\ &- \begin{cases} (\rho \psi^{\text{pol}}(v_\nu - v_\nu))^\pm, & (*) , \\ 0, & (**). \end{cases} \end{aligned}$$

Finally, we remark that evaluation of the electric current in general also requires knowledge of the magnetic field although the magnetic field does not have any influence on the solution of the above system. In order to compute \boldsymbol{B} for a given solution of the above model equations, we assume that magnetization relaxation is fast and hence apply the equilibrium relation obtained in the quasi-magnetostatic case, viz. $\boldsymbol{M} = \frac{\chi_M}{1+\chi_M} \cdot \frac{1}{\mu_0} \boldsymbol{B}$. Then, we have to solve

$$\text{div}(\boldsymbol{B}) = 0, \quad -(1 + \chi) \varepsilon_0 \partial_t (\nabla \varphi) + n^F \boldsymbol{v} + \boldsymbol{J}^F = \frac{1}{\mu_0} \text{curl} \left(\frac{1}{1+\chi_M} \boldsymbol{B} \right), \quad (7.14a)$$

$$\llbracket \boldsymbol{B} \cdot \boldsymbol{\nu} \rrbracket = 0, \quad -\boldsymbol{\nu} \times \llbracket \boldsymbol{v}_s \times ((1 + \chi) \varepsilon_0 \nabla \varphi) \rrbracket + \boldsymbol{J}_s^F = \frac{1}{\mu_0} \boldsymbol{\nu} \times \llbracket \frac{1}{1+\chi_M} \boldsymbol{B} \rrbracket, \quad (7.14b)$$

and can evaluate the electric current as

$$\boldsymbol{j}^e = n^F \boldsymbol{v} + \boldsymbol{J}^F - \partial_t (\chi \varepsilon_0 \nabla \varphi) + \frac{1}{\mu_0} \text{curl} \left(\frac{\chi_M}{1+\chi_M} \boldsymbol{B} \right). \quad (7.15)$$

For paramagnetic and diamagnetic material, typically $|\chi_M| \ll 1$ and thus the Lorentz magnetization is small, such that it often might be appropriate to neglect the magnetic term, making evaluation of the electric current \boldsymbol{j}^e available already without the solution of (7.14).

A Appendix

A.1 Balance of inner energy

Multiplication of the total mass balance by $-\frac{1}{2} |\boldsymbol{v}|^2$, scalar multiplication of the momentum balance by \boldsymbol{v} and subsequent addition yields the balance of kinetic energy

$$\partial_t \left(\frac{1}{2} \rho |\boldsymbol{v}|^2 \right) + \text{div} \left(\frac{1}{2} \rho |\boldsymbol{v}|^2 \boldsymbol{v} - (\boldsymbol{\Sigma} - \boldsymbol{\sigma}^{\text{EM}}) \boldsymbol{v} \right) = - (\boldsymbol{\Sigma} - \boldsymbol{\sigma}^{\text{EM}}) : \nabla \boldsymbol{v} + \rho \boldsymbol{f} \cdot \boldsymbol{v} + \boldsymbol{k} \cdot \boldsymbol{v}, \quad (A.1a)$$

$$\begin{aligned} \partial_{t,\nu} \left(\frac{1}{2} \rho |\boldsymbol{v}|^2 \right) + \left(\frac{1}{2} \rho |\boldsymbol{v}|^2 \right)_{s\tau}^\Delta - \sigma_s^{i\Delta} v_s^i \Big|_\Delta \\ - 2k_M v_\nu \left(\frac{1}{2} \rho |\boldsymbol{v}|^2 \right) &= - \sigma_s^{i\Delta} v_s^i \Big|_\Delta + \rho \boldsymbol{f} \cdot \boldsymbol{v} + \boldsymbol{k} \cdot \boldsymbol{v} & (A.1b) \\ &- \llbracket \frac{1}{2} \rho |\boldsymbol{v}|^2 (v_\nu - v_\nu) - (\boldsymbol{\Sigma} - \boldsymbol{\sigma}^{\text{EM}}) \boldsymbol{v} \cdot \boldsymbol{\nu} \rrbracket \\ &+ \llbracket \frac{1}{2} \rho |\boldsymbol{v} - \boldsymbol{v}_s|^2 (v_\nu - v_\nu) - (\boldsymbol{\Sigma} - \boldsymbol{\sigma}^{\text{EM}}) (\boldsymbol{v} - \boldsymbol{v}_s) \cdot \boldsymbol{\nu} \rrbracket. \end{aligned}$$

Adding the kinetic energy density and inner energy density, we obtain the energy density of matter as $\rho e = \rho u + \frac{1}{2} \rho |\boldsymbol{v}|^2$. Then, the postulation of the total energy of field and matter being a conserved quantity in the absence of gravitation implies the forcing terms in the balance of ρe as the Joule heat

according to (3.7). We split the heat flux as $\mathbf{Q} - \mathbf{q}^{\text{EM}}$ where the second term vanishes in the absence of electromagnetic field.

$$\partial_t(\rho e) + \operatorname{div}(\rho e \mathbf{v} + (\mathbf{Q} - \mathbf{q}^{\text{EM}}) - (\boldsymbol{\Sigma} - \boldsymbol{\sigma}^{\text{EM}})\mathbf{v}) = \pi + \rho \mathbf{f} \cdot \mathbf{v} \quad (\text{A.2a})$$

$$\begin{aligned} \partial_{t,\nu}(\rho e) + \left((\rho e)_{s s} \Delta + q_s^\Delta - \sigma_s^{i\Delta} v_i \right)_{\parallel \Delta} - 2k_M v_\nu (\rho e)_{s s} = \pi + \rho \mathbf{f} \cdot \mathbf{v} \\ - \left[\rho e (v_\nu - v_\nu) + ((\mathbf{Q} - \mathbf{q}^{\text{EM}}) - (\boldsymbol{\Sigma} - \boldsymbol{\sigma}^{\text{EM}})\mathbf{v}) \cdot \boldsymbol{\nu} \right] \end{aligned} \quad (\text{A.2b})$$

Subtracting (A.1) from (A.2) and setting $\mathbf{q}^{\text{EM}} = \boldsymbol{\mathcal{E}} \times \boldsymbol{\mathcal{M}}$ then yields the inner energy balance (4.11). The choice of \mathbf{q}^{EM} is motivated by the fact that it makes the production terms in the inner energy balance directly computable within either of the Galilei limits of the Maxwell equations as demonstrated below, without having to rely on the additional remaining Maxwell equations.

Quasi-electrostatic limit. In the quasi-electrostatic limit, we have $\boldsymbol{\mathcal{E}} = \mathbf{E}$ and it holds

$$\pi - \mathbf{k} \cdot \mathbf{v} = \mathbf{J}^{\text{F}} \cdot \mathbf{E} + \mathbf{J}^{\text{P}} \cdot \mathbf{E}, \quad \pi - \mathbf{k} \cdot \mathbf{v} = \mathbf{J}^{\text{F}} \cdot \bar{\mathbf{E}} + \mathbf{J}^{\text{P}} \cdot \bar{\mathbf{E}}. \quad (\text{A.3})$$

In the volume, we use that in this limit $\operatorname{curl}(\mathbf{E}) = 0$ and apply

$$\mathbf{J}^{\text{P}} \cdot \mathbf{E} = (\partial_t \mathbf{P} + \mathbf{v} \operatorname{div}(\mathbf{P}) + \operatorname{curl}(\boldsymbol{\mathcal{M}}) + \operatorname{curl}(\mathbf{P} \times \mathbf{v})) \cdot \mathbf{E}, \quad (\text{A.4a})$$

$$\operatorname{div}(\boldsymbol{\mathcal{E}} \times \boldsymbol{\mathcal{M}}) = -\operatorname{curl}(\boldsymbol{\mathcal{M}}) \cdot \mathbf{E}, \quad (\text{A.4b})$$

$$\operatorname{curl}(\mathbf{P} \times \mathbf{v}) = \operatorname{div}(\mathbf{v})\mathbf{P} + (\mathbf{v} \cdot \nabla)\mathbf{P} - \operatorname{div}(\mathbf{P})\mathbf{v} - (\mathbf{P} \cdot \nabla)\mathbf{v}, \quad (\text{A.4c})$$

to obtain (4.12a) from

$$\pi - \mathbf{k} \cdot \mathbf{v} + \operatorname{div}(\boldsymbol{\mathcal{E}} \times \boldsymbol{\mathcal{M}}) = \mathbf{J}^{\text{F}} \cdot \mathbf{E} + (\partial_t \mathbf{P} + (\mathbf{v} \cdot \nabla)\mathbf{P}) \cdot \mathbf{E} + \operatorname{div}(\mathbf{v})\mathbf{P} \cdot \mathbf{E} - (\mathbf{P} \cdot \nabla)\mathbf{v} \cdot \mathbf{E}. \quad (\text{A.5})$$

On the surface, we use that $\boldsymbol{\nu} \times \llbracket \mathbf{E} \rrbracket = 0$ and that (3.28) implies

$$\mathbf{J}^{\text{P}} \cdot \bar{\mathbf{E}} = \boldsymbol{\nu} \times \llbracket \boldsymbol{\mathcal{M}} \cdot \mathbf{E} \rrbracket - \boldsymbol{\nu} \times \llbracket ((\mathbf{v} - \mathbf{v}) \times \mathbf{P}) \cdot \mathbf{E} \rrbracket, \quad (\text{A.6})$$

to obtain (4.12b) from

$$\pi - \mathbf{k} \cdot \mathbf{v} + \llbracket \boldsymbol{\mathcal{E}} \times \boldsymbol{\mathcal{M}} \rrbracket \cdot \boldsymbol{\nu} = \mathbf{J}^{\text{F}} \cdot \bar{\mathbf{E}} - \llbracket \mathbf{P} \cdot \boldsymbol{\nu} (\mathbf{v} - \mathbf{v}) \cdot \mathbf{E} - (\mathbf{v} - \mathbf{v}) \cdot \boldsymbol{\nu} \mathbf{P} \cdot \mathbf{E} \rrbracket. \quad (\text{A.7})$$

Quasi-magnetostatic limit. In the quasi-magnetostatic limit, we have $\boldsymbol{\mathcal{M}} = \mathbf{M}$ and it holds

$$\pi - \mathbf{k} \cdot \mathbf{v} = (\mathbf{J}^{\text{F}} + \mathbf{J}^{\text{P}}) \cdot (\mathbf{v} \times \mathbf{B}), \quad \pi - \mathbf{k} \cdot \mathbf{v} = (\mathbf{J}^{\text{F}} + \mathbf{J}^{\text{P}}) \cdot (\mathbf{v} \times \bar{\mathbf{B}}). \quad (\text{A.8})$$

In the volume, we use that $\operatorname{curl}(\mathbf{E}) = -\partial_t \mathbf{B}$ is not small and apply

$$\mathbf{J}^{\text{P}} \cdot (\mathbf{v} \times \mathbf{B}) = \operatorname{curl}(\mathbf{M}) \cdot (\mathbf{v} \times \mathbf{B}), \quad (\text{A.9a})$$

$$\operatorname{div}(\boldsymbol{\mathcal{E}} \times \boldsymbol{\mathcal{M}}) = -(\partial_t \mathbf{B} + \operatorname{curl}(\mathbf{B} \times \mathbf{v})) \cdot \mathbf{M} - \operatorname{curl}(\mathbf{M}) \cdot (\mathbf{v} \times \mathbf{B}), \quad (\text{A.9b})$$

$$\operatorname{curl}(\mathbf{B} \times \mathbf{v}) = \operatorname{div}(\mathbf{v})\mathbf{B} + (\mathbf{v} \cdot \nabla)\mathbf{B} - (\mathbf{B} \cdot \nabla)\mathbf{v}, \quad (\text{A.9c})$$

to obtain (4.13a) from

$$\pi - \mathbf{k} \cdot \mathbf{v} + \operatorname{div}(\boldsymbol{\mathcal{E}} \times \boldsymbol{\mathcal{M}}) = \mathbf{J}^{\text{F}} \cdot (\mathbf{v} \times \mathbf{B}) - (\partial_t \mathbf{B} + (\mathbf{v} \cdot \nabla)\mathbf{B}) \cdot \mathbf{M} - \operatorname{div}(\mathbf{v})\mathbf{B} \cdot \mathbf{M} + (\mathbf{B} \cdot \nabla)\mathbf{v} \cdot \mathbf{M}. \quad (\text{A.10})$$

On the surface, we use $\boldsymbol{\nu} \times \llbracket \boldsymbol{v} \times \boldsymbol{B} \rrbracket = 0$ and

$$\begin{aligned} \boldsymbol{J}_s^P \cdot (\boldsymbol{v}_s \times \bar{\boldsymbol{B}}) &= \boldsymbol{\nu} \times \llbracket \boldsymbol{M} \rrbracket \cdot (\boldsymbol{v}_s \times \bar{\boldsymbol{B}}) = \boldsymbol{\nu} \times \llbracket \boldsymbol{M} \cdot (\boldsymbol{v}_s \times \boldsymbol{B}) \rrbracket \\ &= \boldsymbol{\nu} \times \llbracket \boldsymbol{M} \cdot (\boldsymbol{v} \times \boldsymbol{B}) \rrbracket - \boldsymbol{\nu} \times \llbracket \boldsymbol{M} \cdot ((\boldsymbol{v} - \boldsymbol{v}_s) \times \boldsymbol{B}) \rrbracket \\ &= \boldsymbol{\nu} \times \llbracket \boldsymbol{M} \cdot \boldsymbol{\mathcal{E}} \rrbracket - \boldsymbol{\nu} \times \llbracket ((\boldsymbol{v} - \boldsymbol{v}_s) \times \boldsymbol{B}) \cdot \boldsymbol{M} \rrbracket \end{aligned} \quad (\text{A.11})$$

to obtain (4.13b) from

$$\pi_s - \boldsymbol{k}_s \cdot \boldsymbol{v}_s + \llbracket \boldsymbol{\mathcal{E}} \times \boldsymbol{\mathcal{M}} \rrbracket \cdot \boldsymbol{\nu} = \boldsymbol{J}_s^F \cdot (\boldsymbol{v}_s \times \bar{\boldsymbol{B}}) - \llbracket \boldsymbol{B} \cdot \boldsymbol{\nu} (\boldsymbol{v} - \boldsymbol{v}_s) \cdot \boldsymbol{M} - (\boldsymbol{v} - \boldsymbol{v}_s) \cdot \boldsymbol{\nu} \boldsymbol{B} \cdot \boldsymbol{M} \rrbracket. \quad (\text{A.12})$$

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