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Modeling of electrochemical double layers
in thermodynamic non-equilibrium

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Abstract

We consider the contact between an electrolyte and a solid electrode. At first we formulate a thermodynamic consistent model that resolves boundary layers at interfaces. The model includes charge transport, diffusion, chemical reactions, viscosity, elasticity and polarization under isothermal conditions. There is a coupling between these phenomena that particularly involves the local pressure in the electrolyte. Therefore the momentum balance is of major importance for the correct description of the boundary layers.

The width of the boundary layers is typically very small compared to the macroscopic dimensions of the system. In a second step we thus apply the method of asymptotic analysis to derive a simpler reduced model that does not resolve the boundary layers but instead incorporates the electrochemical properties of the layers into a set of new boundary conditions.

With the reduced model, we analyze the double layer capacitance for a metal–electrolyte interface.

1 Introduction

Whenever two electronic and ionic conductors are brought in contact to each other, electric double layers are formed at the interface between these two materials. A physically and mathematically consistent description of these double layers is crucial for the understanding and improvement of systems for energy transformation and storage like fuel cells and batteries.

There is a comprehensive and well established literature on electrochemical double layers, see e.g. standard textbooks [NTA04, BRGA02]. However, an approach that fully relies on non-equilibrium continuum thermodynamics [dM63, Mül85] is missing. Instead, the electrochemical standard theory uses only certain parts of thermodynamics and then introduces ad hoc assumptions based on very special experimental circumstances to close the system of model equations. In many cases this procedure leads to thermodynamic and conceptual inconsistencies and impedes the transfer of existing models to novel electrochemical systems.

From a historically point of view the shortcomings of the classical theory are obvious. The theoretical foundations of electrochemistry were laid down in the end of the 19th century by M. Planck [Pla90a, Pla90b] and W. Nernst [Ner89] and more or less completed in the thirties of the 20th century [Ste24, But24a, But24b, EGV30, EGV31, Fru33, Gra47]. However, a thermodynamically consistent continuum theory was first developed ten years later by C. Eckard [Eck40a, Eck40b] and J. Meixner [Mei43]. The first standard textbook on "Non-Equilibrium Thermodynamics" was published by S. de Groot and P. Mazur in 1963 [dM63]. Particularly the transfer of continuum thermodynamics to a system of surfaces separating different bulk bodies was started in the eighties by I. Müller [Mül85], K. Hutter [AH88a, AH88b, AH88c] and D. Bedeaux [ABM75, Bed86].

The results obtained by Müller, Hutter and Bedeaux are only rarely noticed in electrochemistry. The main reason might be the complexity of the equations of continuum physics. For example, experimental studies show that the magnetic field and the macroscopic kinetic energy density of the involved particles only play a minor role. However, in order to end up with a consistent mathematical model, these quantities must at first be incorporated, i.e. at first the complete set of Maxwell's equations and of the balance equations for matter, particularly the total energy balance and the momentum balance, must be taken into account. A further reason is that some accepted relations of classical electrochemistry are not directly found in the equations of continuum thermodynamics of charged matter. For example, the Butler-Volmer equation relates the electron transfer reaction rates at the interface to the corresponding electric potential difference. To the contrary, in the equations of thermodynamics exclusively the electric field \mathbf{E} but not its potential φ , with $\mathbf{E} = -\nabla\varphi$, explicitly appears. One approach to resolve this apparent antagonism is the introduction of mesoscopic thermodynamics by J.M. Rubi and S. Kjelstrup [RK03].

In this paper we generalize the model of [DGM13] to include chemical reactions and surface equations. But we keep some of the simplifying assumptions like electrostatic and isothermal approximation. The model gives a detailed local description of the interface and its neighborhood. Compared to standard models, the complexity of our "*complete*" model can largely be attributed to the inclusion of momentum balance equation for the barycentric velocity. Then we use the method of formal asymptotic analysis to simplify the complexity of the complete model and derive a "*reduced*" model which is much closer to familiar models of electrochemistry. The reduced model is characterized by local charge neutrality and a simpler relation between the electric current and the electric field. Moreover, the original surface equations at the interface S uniquely imply new surface equations at the (double-layer) interface I . This result is the essential contribution of our approach. The reduced models even allow to recover well known relations of classical electrochemistry like general equations of Butler-Volmer type.

Figure 1 serves to exhibit both the subtleties of the problem and our solution strategies. Here we consider an electrolyte and a solid electrode. The domains of the electrode, the electrolyte and their (actual) interface are indicated by Ω^+ , Ω^- and S , respectively. Figure 1_{left} shows the one-dimensional setup. From left to right we have the electrode (yellow), the interface (dashed black line) and the electrolyte (gray). Electrode and electrolyte are described as mixtures consisting of various constituents. The interface S itself also may be a carrier of constituents and is thus considered as a substance. Each of the three substances are described by a mixture model relying on equations of balance for the two bulk domains while on the interface we have jump conditions that are derived from surface balance equations.

Figure 1_{left} shows the possible behavior of a generic field u from our list of state variables. In the bulk domains on the left and right sides of the interface we observe the indicated variation. Across the interface S the field u has a discontinuity described by the double bracket $[[u]]$.

The field equations for the variables contain a small and positive parameter λ . The parameter λ implies that rapid variations of u are restricted to a small neighborhood of the interface S . In other words, the parameter λ induces boundary layers on the left and right sides of S . Let L^{ref} be a typical length scale of the system, then λL^{ref} characterizes the width of the layers and is known as the Debye length. This fact is indicated in Figure 1_{middle}. Two different expansions of the variable u are introduced: for the approximation inside the boundary layers one defines an

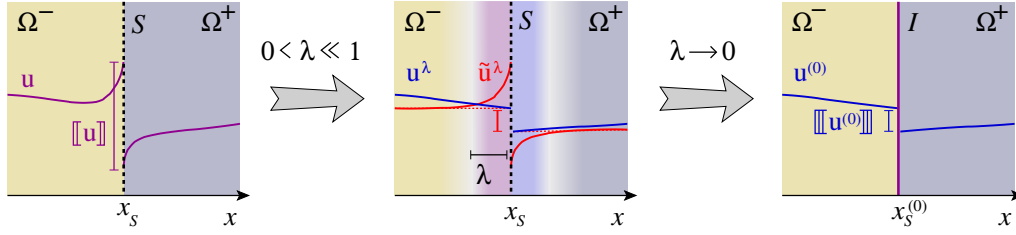


Figure 1: Generic field variable u for an electrochemical system of two substances in contact with the interface S (left). Boundary layers due to a small parameter λ in the model equations (middle). In a simplified model for $\lambda \rightarrow 0$, modified jump conditions contain the relevant information of the double layer that is not resolved any more.

expansion \tilde{u}^λ in terms of rescaled variables. In the bulk part a different approximation u^λ is used.

One of the main objectives of this study is the description of the mathematical limit $\lambda \rightarrow 0$. In this case already the leading order term $u^{(0)}$ of the expansion u^λ is an accurate approximation of u in the whole bulk regions Ω^\pm and thus gives rise to a meaningful jump at the interface at $x_S^{(0)}$ as indicated in Figure 1_{right}. An important result of our analysis is, that from the leading order terms we get a closed set of model equations that consistently incorporates the effect of the boundary layers without the need to determine \tilde{u}^λ . If the boundary layers are of interest, the limit $\lambda \rightarrow 0$ also provides an additional closed set of equations to determine the leading order quantities $\tilde{u}^{(0)}$. To distinguish from the original model with $\lambda > 0$ we denote in the limit $\lambda \rightarrow 0$ the interface by I instead of S and denote the jump of $u^{(0)}$ at I by a triple bracket $\llbracket u^{(0)} \rrbracket$ instead of using the double bracket. When studying the reduced models alone, we will skip the superscript (0) for simplicity of notation.

Outline In the following section, a thermodynamically consistent complete model for electrochemical systems in contact with interfaces is presented. In Section 3 we introduce a scaling in terms of the small parameter λ in order to carry out the formal asymptotic analysis in Section 4. The resulting limiting models are summarized and discussed in Section 5. Finally in Section 6 we apply the models to describe an ideal polarizable electrode.

2 Thermodynamically consistent modeling of mixtures separated by an electrochemical interface

2.1 Basic Assumptions

To limit the complexity of the model, we first formulate simplifying assumptions appropriate for macroscopic electrochemical system for energy storage or -conversion. Systems of nanometer size or high frequency oscillations may require the inclusion of finer scales and will in general lead to a different scaling for the asymptotic analysis.

2.1.1 Length scales

In equilibrium the species concentrations and the electrostatic potential exhibit boundary layers whose width is related to the well known Debye-length. This length scale necessarily has to be included in the model and defines the smallest length scale to be considered here.

2.1.2 Assumptions on domain geometry

We consider an interface S dividing a domain $\Omega \subset \mathbb{R}^3$ into two subdomains $\Omega^\pm \subseteq \mathbb{R}^3$ with $S := \partial\Omega^+ \cap \partial\Omega^-$. The surface normal is chosen to be the inner normal of Ω^+ . There are no contact lines or triple points between several bulk domains, but in general Ω^+ still can have arbitrary shape. Since we are interested in macroscopic systems with a typical size much larger than the Debye length, we can simplify the geometric properties of the interface by assuming that S is planar and lies parallel to the coordinate plane (x_2, x_3) whose normal vector $\boldsymbol{\nu}$ is oriented in x_1 direction. This means we use a quasi-one-dimensional approximation for the surface.

2.1.3 Assumptions on the interfaces

In the quasi-one-dimensional setting for the surface we may assume that there are no tangential fluxes of mass, momentum, energy or charge. The interface velocity \boldsymbol{w} lies in normal direction $\boldsymbol{w} = w_\nu \boldsymbol{\nu}$. Given a parametrization $(t, x_2, x_3) \rightarrow (x_S(t), x_2, x_3)$ of the interfaces S , we have

$$\boldsymbol{w} = w_\nu \boldsymbol{\nu} = \frac{dx_S}{dt} \boldsymbol{\nu}. \quad (1)$$

2.1.4 Quasi-static electric field

In the context of electrochemical systems it is customary to use the electrostatic approximation, i.e. one takes into account only the electric field while the magnetic field is ignored. We consider quasi-static electric fields only.

All constituents may consist of polarizable matter, but magnetization is not considered here. Polarization embodies phenomena caused by microscopic charges, for example, atomic dipoles within atoms and molecules.

2.1.5 Time scales

Mechanical relaxation takes place on the time scale of sound wave propagation. A detailed analysis of all possible time scales reveals that this time scale is much faster than the time scale of the electrostatic approximation, cf. [Guh15]. Hence it suffices to account for the quasi-static momentum balance.

2.1.6 Isothermal case

We only consider isothermal processes. Hence the bulk temperature T and surface temperature T_s will only appear as a constant parameters in the constitutive equations satisfying $T = T_s$.

2.2 Description of the reacting mixtures

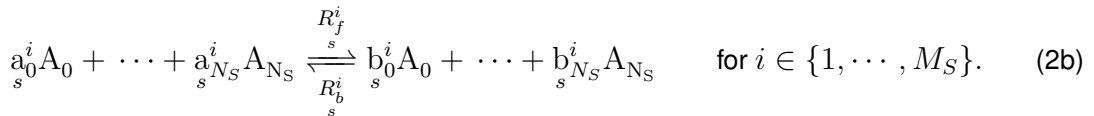
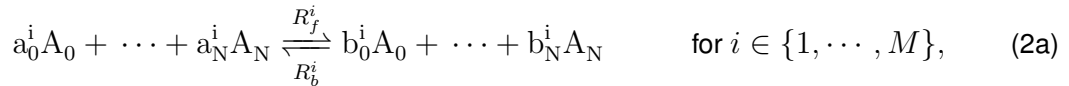
For quantities defined in the domains Ω^+ or Ω^- there will often be corresponding quantities on the interfaces S . As a convention the same letters are used for these quantities but the surface variables are indicated by a subscript s .

Constituents and chemical reactions In each of the two domains Ω^+ and Ω^- and on the interface S , we consider a mixture of several constituents. For simplicity of notation we only indicate whether quantities are defined in Ω^- or Ω^+ by the signs $-$ or $+$ if necessary. The total number of constituents in Ω^\pm is denoted by $N + 1$ and the set of constituents is $\mathcal{M} = \{A_0, A_1, \dots, A_N\}$, usually indexed by $\alpha \in \{0, 1, \dots, N\}$.

All constituents in one of the subdomains Ω^\pm are also assumed to be constituents on the surface S but in addition there may be some constituents that are exclusively present on S . Accordingly, there are $N_S + 1$ constituents on the surface S that are represented by the set $\mathcal{M}_s = \{A_0, A_1, \dots, A_{N_S}\}$.

A constituent A_α has the (atomic) mass m_α and may be carrier of the charge $z_\alpha e_0$, where the positive constant e_0 is the elementary charge and z_α is the charge number of the constituent.

There may be M chemical reactions among the bulk constituents and M_S chemical reactions on the surface. These reactions may be written in the general form



The constants a_α^i, b_α^i are positive integers and $\gamma_\alpha^i := b_\alpha^i - a_\alpha^i$ denote the stoichiometric coefficients of the reactions. The reaction from left to right is called forward reaction with reaction rate $R_f^i > 0$. The reaction in the reverse direction with rate $R_b^i > 0$ is the backward reaction. The net reaction rate is defined as $R^i = R_f^i - R_b^i$. Since charge and mass have to be conserved by every single reaction in the bulk and on the surface, we have

$$\sum_{\alpha=0}^N z_\alpha \gamma_\alpha^i = 0 \quad \text{and} \quad \sum_{\alpha=0}^{N_S} z_\alpha \gamma_\alpha^i = 0, \quad (3a)$$

$$\sum_{\alpha=0}^N m_\alpha \gamma_\alpha^i = 0 \quad \text{and} \quad \sum_{\alpha=0}^{N_S} m_\alpha \gamma_\alpha^i = 0. \quad (3b)$$

Basic quantities In the isothermal case, the thermodynamic state of Ω^\pm at any time t is described by the number densities $(n_\alpha)_{\alpha=0,1,\dots,N}$, the velocities $(\mathbf{v}_\alpha)_{\alpha=0,1,\dots,N}$ of the constituents and the electric field \mathbf{E} . Analogously, the thermodynamic state of the interface S is characterized by the number densities of the interfacial constituents, $(n_\alpha)_s)_{\alpha=0,1,\dots,N_S}$ and the interface speed w .

In general, the introduced quantities may be functions of time $t \geq 0$ and space $x \in \mathbb{R}^3$. On S , the basic variables are functions of time only, due to the interfacial assumptions above. Multiplication of the number densities n_α and partial velocities \mathbf{v}_α by m_α gives the partial mass densities and mass fluxes:

$$\rho_\alpha = m_\alpha n_\alpha \quad \text{and} \quad \mathbf{j}_\alpha = \rho_\alpha \mathbf{v}_\alpha, \quad (4a)$$

$$\rho_\alpha = m_\alpha n_\alpha. \quad (4b)$$

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

$$\rho = \sum_{\alpha=0}^N \rho_\alpha \quad \text{and} \quad \mathbf{v} = \frac{1}{\rho} \sum_{\alpha=0}^N \rho_\alpha \mathbf{v}_\alpha, \quad (5a)$$

$$\rho_s = \sum_{\alpha=0}^{N_S} \rho_\alpha. \quad (5b)$$

Total free charge density and total free current are calculated by

$$n^F = \sum_{\alpha=0}^N z_\alpha e_0 n_\alpha \quad \text{and} \quad \mathbf{j}^F = \sum_{\alpha=0}^N \frac{e_0 z_\alpha}{m_\alpha} \mathbf{j}_\alpha, \quad (6a)$$

$$n_s^F = \sum_{\alpha=0}^{N_S} z_\alpha e_0 n_\alpha. \quad (6b)$$

The application of Maxwell's theory to continuous matter shows that the total electric charge density n^e and the total electric current \mathbf{j}^e consist of two additive contributions. Besides free charge densities and free currents, there are charge densities and currents due to polarization. We write

$$n^e = n^F + n^P \quad \text{and} \quad \mathbf{j}^e = \mathbf{j}^F + \mathbf{j}^P, \quad (7a)$$

$$n_s^e = n_s^F + n_s^P. \quad (7b)$$

2.3 Model equations

The coupled system of equations for the basic variables rely on equations of balance for the partial mass of the constituents and the momentum of the mixture and the Maxwell equations. In addition there are associated interface conditions which are derived from surface balance equations. We introduce the boundary values and the jump of a generic function $u(t, x)$ in Ω^\pm across the interface. We define

$$u|_S^\pm = \lim_{x \in \Omega^\pm \rightarrow S} u \quad \text{and} \quad \llbracket u \rrbracket = u|_S^+ - u|_S^-. \quad (8)$$

If the function u is not defined in Ω^+ or Ω^- , we set the corresponding value in (8) to zero.

Equations for the electric field Under the assumptions above, the Maxwell equations in the bulk regions and for interfaces reduce to

$$\operatorname{curl}(\mathbf{E}) = 0, \quad \llbracket \mathbf{E} \times \boldsymbol{\nu} \rrbracket = 0, \quad (9a)$$

$$\varepsilon_0 \operatorname{div}(\mathbf{E}) = n^F + n^P, \quad \varepsilon_0 \llbracket \mathbf{E} \cdot \boldsymbol{\nu} \rrbracket = n_s^F + n_s^P, \quad (9b)$$

$$-\operatorname{div}(\mathbf{P}) = n^P, \quad -\llbracket \mathbf{P} \cdot \boldsymbol{\nu} \rrbracket = n_s^P, \quad (9c)$$

$$\partial_t \mathbf{P} + \operatorname{curl}(\mathbf{P} \times \mathbf{v}) = \mathbf{j}^P, \quad \boldsymbol{\nu} \times \llbracket (\mathbf{v} - \mathbf{w}) \times \mathbf{P} \rrbracket = 0, \quad (9d)$$

where \mathbf{P} denotes the vector of polarization, cf. [Mül85]. Recall that on the interfaces we ignore tangential currents. There are only normal currents across the interface, which leads to the simple law (9d) for the polarization charge. Because of (9a), there is a representation of \mathbf{E} as

$$\mathbf{E} = -\nabla \varphi, \quad (10)$$

The interface condition of (9a) implies that a jump of φ at S is spacially constant. The constant turns out to be independent of the two materials adjacent to S . Therefore, we choose

$$\llbracket \varphi \rrbracket = 0, \quad \text{leading to} \quad \varphi := \varphi|_S^+ = \varphi|_S^-. \quad (11)$$

Thus we assume that the interface itself is not a double layer, i.e. there is no surface density of dipoles on S .

Equations of balance In the bulk, we define the diffusion flux \mathbf{J}_α of constituent A_α as

$$\mathbf{J}_\alpha = \rho_\alpha (\mathbf{v}_\alpha - \mathbf{v}) \quad \text{implying} \quad \sum_{\alpha=0}^N \mathbf{J}_\alpha = 0. \quad (12)$$

Thus the mass flux of constituent A_α is split into $\dot{\mathbf{j}}_\alpha = \rho_\alpha \mathbf{v} + \mathbf{J}_\alpha$. In each of the subdomains Ω^\pm as well as on the interface S , the partial mass balances may be written as

$$\partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha \mathbf{v} + \mathbf{J}_\alpha) = r_\alpha, \quad \text{for } \alpha = 0, 1, \dots, N, \quad (13a)$$

$$\partial_t \rho_\alpha + \llbracket (\rho_\alpha (\mathbf{v} - \mathbf{w}) + \mathbf{J}_\alpha) \cdot \boldsymbol{\nu} \rrbracket = r_\alpha, \quad \text{for } \alpha = 0, 1, \dots, N_S. \quad (13b)$$

Herein r_α and r_α denote the mass production rate of constituent A_α . We have

$$r_\alpha = \sum_{i=1}^M m_\alpha \gamma_\alpha^i R^i, \quad r_\alpha = \sum_{i=1}^{M_S} m_\alpha \gamma_\alpha^i R_s^i. \quad (14)$$

The conservation of mass for every single reaction according (3b) implies

$$\sum_{\alpha=0}^N r_\alpha = 0 \quad \text{and} \quad \sum_{\alpha=0}^{N_S} r_\alpha = 0. \quad (15)$$

The quasi-static balance equations for momentum read

$$-\operatorname{div}(\boldsymbol{\Sigma}) = \rho \mathbf{b}, \quad (16a)$$

$$-\llbracket \boldsymbol{\nu}^T \cdot \boldsymbol{\Sigma} \cdot \boldsymbol{\nu} \rrbracket = \boldsymbol{\nu}^T \cdot \rho \mathbf{b}_s, \quad (16b)$$

where $\boldsymbol{\Sigma} := \boldsymbol{\sigma} + \varepsilon_0(\mathbf{E} \otimes \mathbf{E} - \frac{1}{2}|\mathbf{E}|^2 \mathbf{1})$ is the total stress consisting of a material part given by the symmetric Cauchy stress tensor $\boldsymbol{\sigma}$ and the Maxwell stress due to quasi-static Lorentz forces, cf. [dM63, Mül85]. $\mathbf{1}$ denotes the unit matrix. The force densities $\rho \mathbf{b}$ and $\rho \mathbf{b}_s$ are due to gravitation. In the following we set $\mathbf{b} = \mathbf{b}_s = 0$.

Variants of the equations of balance There are useful alternatives of the equations of balance. Instead of the $N + 1$ partial mass balances we use the mass balance for the total mass density of the mixture and the remaining N mass balances serve as the basis for the diffusion equations,

$$\partial_t \rho_\alpha + \operatorname{div}(\rho_\alpha \mathbf{v} + \mathbf{J}_\alpha) = r_\alpha \quad \text{for } \alpha = 1, \dots, N, \quad (17a)$$

$$\partial_t \rho + \operatorname{div}(\rho \mathbf{v}) = 0. \quad (17b)$$

Summing up the partial mass balances yields the interfacial balance for the total mass density,

$$\partial_t \rho_\alpha + \llbracket (\rho_\alpha (\mathbf{v} - \mathbf{w}) + \mathbf{J}_\alpha) \cdot \boldsymbol{\nu} \rrbracket = r_\alpha \quad \text{for } \alpha = 1, \dots, N_S, \quad (17c)$$

$$\partial_t \rho + \llbracket \rho (\mathbf{v} - \mathbf{w}) \cdot \boldsymbol{\nu} \rrbracket = 0. \quad (17d)$$

2.4 Balance equation of electric charge

From the bulk equations (9a)₁–(9d)₁ and (13a) we conclude that electric charge density and electric current satisfy the conservation law

$$\partial_t n^e + \operatorname{div}(\mathbf{j}^e) = 0. \quad (18)$$

The volume equations (6a)–(9d) imply the representation

$$\mathbf{j}^e = \sum_{\alpha=0}^N z_\alpha e_0 n_\alpha \mathbf{v} + \sum_{\alpha=0}^N \frac{z_\alpha e_0}{m_\alpha} \mathbf{J}_\alpha + \partial_t \mathbf{P} + \operatorname{curl}(\mathbf{P} \times \mathbf{v}). \quad (19)$$

Thus an electric current is generated by three phenomena: i) convection of free charges, ii) diffusion of free charges and iii) polarization. Similarly we conclude from the interfacial equations (9a)–(9d) and (13b) that the interfacial charge density n_s^e satisfies

$$\partial_t n_s^e + \llbracket (\mathbf{j}^e - n_s^e \mathbf{w}) \cdot \boldsymbol{\nu} \rrbracket = 0. \quad (20)$$

2.5 Constitutive model

The variables $(\rho_\alpha)_{\alpha=0,1,\dots,N}$, \mathbf{v} and \mathbf{E} are not the only quantities in the equations of balance. There are further quantities, e.g. diffusion fluxes and production rates, that must be given by thermodynamically consistent constitutive equations, such that the equations of balance become a system of partial differential equations for the variables. Our constitutive model describes a viscous-elastic, reacting and polarizable mixture with volume changes and diffusion under isothermal conditions.

Free energy, chemical potentials and polarization vector In order to embody a wide class of different materials we use free energy functions of the general form

$$\rho\psi = \rho\psi(T, \rho_0, \rho_1, \dots, \rho_N, \mathbf{E}) \quad \text{and} \quad \rho_s\psi = \rho_s\psi(T, \rho_0, \rho_1, \dots, \rho_{N_s}). \quad (21)$$

In contrast to the bulk the electric field does not appear in the surface free energy. This reflects our assumption that interfacial polarization charges are exclusively induced due to different polarizations of the bulk phases as it is described by the jump condition (9c).

In isothermal processes, the temperatures T and T_s are constant and identical. The chemical potentials of the bulk and surface materials and the polarization vector in the bulk are defined by means of the free energies, i.e.

$$\mu_\alpha = \frac{\partial \rho\psi}{\partial \rho_\alpha}, \quad \mu_\alpha^s = \frac{\partial \rho_s\psi}{\partial \rho_\alpha^s} \quad \text{and} \quad \mathbf{P} = -\frac{\partial \rho\psi}{\partial \mathbf{E}}. \quad (22)$$

Constitutive model in Ω^\pm We start with a representation of the isothermal entropy production due to (i) diffusion, (ii) chemical reactions and (iii) viscous flow:

$$\begin{aligned} \xi = & -\sum_{\alpha=0}^N \mathbf{J}_\alpha \left(\nabla \left(\frac{\mu_\alpha}{T} \right) + \frac{1}{T} \frac{z_\alpha e_0}{m_\alpha} \mathbf{E} \right) - \frac{1}{T} \sum_{i=1}^M \left(\sum_{\alpha=0}^N m_\alpha \gamma_\alpha^i \mu_\alpha \right) R^i \\ & + \frac{1}{T} \left(\boldsymbol{\sigma} - \mathbf{E} \otimes \mathbf{P} - (\rho\psi - \sum_{\alpha=1}^N \rho_\alpha \mu_\alpha) \mathbf{1} \right) : \frac{1}{2} (\nabla \mathbf{v} + \nabla \mathbf{v}^T). \end{aligned} \quad (23)$$

The representation of the entropy production is based on the general free energies (21). The entropy production is in accordance to the 2nd law of thermodynamics, if it is non negative for every solution of the balance equations, $\xi \geq 0$, and if equilibrium is a solution of the balance equations with $\xi = 0$. The derivation of the entropy production may be found in [dM63, Guh15, MR59, Mül85].

The representation of ξ is important because it allows to formulate constitutive relations for the diffusion fluxes, the reaction rates and the stress tensor that guarantee $\xi \geq 0$. In this case we say that the constitutive functions are compatible with the 2nd law of thermodynamics.

The simplest choice of constitutive functions for N diffusion fluxes $(\mathbf{J}_\alpha)_{\alpha=1,\dots,N}$ are

$$\mathbf{J}_\alpha = - \sum_{\beta=1}^N M_{\alpha\beta} \left(\nabla \left(\frac{\mu_\beta - \mu_0}{T} \right) - \frac{1}{T} \left(\frac{z_\beta e_0}{m_\beta} - \frac{z_0 e_0}{m_0} \right) \mathbf{E} \right), \quad \alpha = 1, \dots, N. \quad (24)$$

The kinetic coefficients $M_{\alpha\beta}$ define the mobility matrix that must be positive definite. It is important to note that there are only N independent diffusion fluxes, because due to the side condition (6a), the flux \mathbf{J}_0 is already given by the other N fluxes according to $\mathbf{J}_0 = - \sum_{\alpha=1}^N \mathbf{J}_\alpha$.

The constitutive equation for the stress tensor is constructed in an analogous manner [dM63, Mül85],

$$\boldsymbol{\sigma} = (\rho\psi - \sum_{\alpha=0}^N \rho_\alpha \mu_\alpha) \mathbf{1} + \mathbf{E} \otimes \mathbf{P} + \nu \operatorname{div}(\mathbf{v}) \mathbf{1} + \eta (\nabla \mathbf{v} + \nabla \mathbf{v}^T) \\ \text{with } \nu + \frac{2}{3}\eta \geq 0 \quad \text{and } \eta \geq 0, \quad (25)$$

where ν is the bulk viscosity and η denotes the shear viscosity. Both viscosities are considered as constants here.

Chemical reactions are typically far from equilibrium and show an Arrhenius type exponential dependency on the driving force. Thus, we choose the following nonlinear relation for the reaction rates that guarantees a non-negative entropy production in (23):

$$R^i = L^i \left[1 - \exp \left(\frac{A^i}{kT} \sum_{\alpha=0}^N \gamma_\alpha^i m_\alpha \mu_\alpha \right) \right] \quad \text{with } A^i, L^i \geq 0. \quad (26)$$

Herein A^i and L^i are introduced as further phenomenological constants. To have a symmetric form of the reaction rates $R^i = R_f^i - R_b^i$ and analogous dependencies for the forward and backward reaction we set

$$L^i = R_0^i \exp \left(-\beta^i \frac{A^i}{kT} \sum_{\alpha=0}^N \gamma_\alpha^i m_\alpha \mu_\alpha \right) \quad \text{with } R_0^i \geq 0. \quad (27)$$

with constants β^i that are called symmetry factors.

For a more detailed discussion of chemical reactions in the context of the 2nd law of thermodynamics we refer the reader to [BD14, Guh15].

Constitutive model on \mathcal{S} As in the bulk, further quantities must be given by thermodynamically consistent constitutive equations. The exploitation of the general function (21) by the axioms of the 2nd law of thermodynamics for interfaces implies the following representation and sign of the

interfacial entropy production in the isothermal case, cf. [Mül85, AB87, Guh15]:

$$\begin{aligned}
\xi_s = & \frac{1}{T_s} \left[\boldsymbol{\nu} \cdot \left(\boldsymbol{\sigma} - \mathbf{E} \otimes \mathbf{P} - \left(\rho\psi - \sum_{\alpha=0}^N \rho_\alpha \mu_\alpha \right) \mathbf{1} - T_s \rho \left(\frac{\mu_0}{T} - \frac{\mu_0}{T_s} \right) \mathbf{1} \right) \cdot (\mathbf{v} - \mathbf{w}) \right] \\
& - \left[\sum_{\alpha=1}^N \left(\frac{\mu_\alpha - \mu_0}{T} - \frac{\mu_\alpha - \mu_0}{T_s} \right) (\rho_\alpha (\mathbf{v} - \mathbf{w}) + \mathbf{J}_\alpha) \cdot \boldsymbol{\nu} \right] \\
& - \frac{1}{T_s} \sum_{i=1}^{M_S} \left(\sum_{\alpha=0}^{N_S} \gamma_\alpha^i m_\alpha \mu_\alpha \right) R_s^i \geq 0. \tag{28}
\end{aligned}$$

The interfacial entropy production ξ_s must be non negative for every solution of the balance equations. Interfacial equilibrium is a solution of the balance equations with $\xi_s = 0$.

Due to the assumptions above, there are only three dissipative mechanisms, namely viscosity due to normal mass transport, adsorption/desorption of species on the interface S and chemical reaction on S .

The chemical contribution to the interfacial entropy production (28) is formally the same as in the bulk. Hence in analogy to (26) we postulate the nonlinear relation

$$R_s^i = L_s^i \left[1 - \exp \left(\frac{A_s^i}{kT} \sum_{\alpha=0}^{N_S} \gamma_\alpha^i m_\alpha \mu_\alpha \right) \right] \quad \text{with } A_s^i, L_s^i \geq 0, \tag{29a}$$

$$L_s^i = R_s^i \exp \left(-\beta_s^i \frac{A_s^i}{kT} \sum_{\alpha=0}^{N_S} \gamma_\alpha^i m_\alpha \mu_\alpha \right), \quad \text{with } R_s^i \geq 0. \tag{29b}$$

The quantities $A_s^i, L_s^i, R_s^i \geq 0$ and β_s^i are phenomenological coefficients. The constant coefficients β_s^i are called symmetry factors of the surface reactions.

For the adsorption process on S we choose following constitutive functions for the normal diffusion fluxes at the surface

$$(\rho_\alpha^\pm (\mathbf{v} - \mathbf{w})^\pm + \mathbf{J}_\alpha^\pm) \cdot \boldsymbol{\nu} = \mp \sum_{\beta=1}^N M_{\alpha\beta}^\pm \left(\frac{\mu_\beta^\pm - \mu_0^\pm}{T} - \frac{\mu_\beta - \mu_0}{T_s} \right). \tag{30}$$

This leads to a corresponding non-negative entropy production. For the same reason we choose for the normal stress

$$\begin{aligned}
& \boldsymbol{\nu} \cdot \left(\boldsymbol{\sigma} - \mathbf{E} \otimes \mathbf{P} \right)^\pm \cdot \boldsymbol{\nu} - \left(\rho\psi - \sum_{\alpha=0}^N \rho_\alpha \mu_\alpha \right)^\pm - T_s \rho \left(\frac{\mu_0}{T} - \frac{\mu_0}{T_s} \right)^\pm \\
& = \pm L_s^\pm (\rho^2 (\mathbf{v} - \mathbf{w}))^\pm \cdot \boldsymbol{\nu}. \tag{31}
\end{aligned}$$

The phenomenological matrix $M_{\alpha\beta}^\pm$ is positive definite and the coefficients L_s^\pm are positive constants.

Due to the assumption on the geometry 2.1, in the entropy production (28) there are no contributions related to tangential fluxes of mass, momentum and energy. In particular we obtain no contribution due to surface tension. Nevertheless surface tension is of importance for planar surfaces and we define

$$\sigma_s = \rho_s \psi_s - \sum_{\alpha=0}^{N_S} \rho_{\alpha s} \mu_{\alpha s}. \quad (32)$$

A derivation of a constitutive relation justifying this definition (32) is only possible in the context of arbitrary curved surfaces, e.g. see [Mül85, Guh15].

Further constitutive assumptions Up to now the constitutive model is quite general. The specific material properties for the mixture at hand are embodied in the free energy functions (21) and the phenomenological coefficients. In the following we restrict the generality of free energy function (21)₁ by assuming a simple dependence on the electric field, viz.

$$\rho \psi = \rho \hat{\psi}(T, \rho_1, \rho_2, \dots, \rho_N) - \frac{1}{2} \varepsilon_0 \chi \mathbf{E}^2, \quad (33)$$

with a constant electric susceptibility χ . This ansatz implies a simple polarization model where the polarization is proportional to the electric field because from (22)₂ we obtain $\mathbf{P} = \varepsilon_0 \chi \mathbf{E}$. The constancy of χ implies that the combination $\rho \hat{\psi} - \sum_{\alpha=0}^N \rho_{\alpha} \mu_{\alpha}$ does not depend on the electric field. Therefore the quantity

$$p = -\rho \hat{\psi} + \sum_{\alpha=0}^N \rho_{\alpha} \mu_{\alpha} \quad (34)$$

is called the elastic part of the pressure and (34) is called the Gibbs-Duhem equation.

3 Dimensionless form of the model

In preparation of the formal asymptotic analysis of the next section it is necessary to transform the equations into a dimensionless form and to identify the small parameters of the system.

3.1 Scaling to dimensionless quantities

Dimensionless quantities We introduce scaling constants L^{ref} , t^{ref} , n^{ref} and m^{ref} that are related to characteristic length, time, number density and molecular weight. Then, we substitute in the bulk regions Ω^{\pm} :

$$\begin{aligned} \mathbf{x} &\rightarrow L^{ref} \mathbf{x}, & t &\rightarrow t^{ref} t, & \mathbf{v} &\rightarrow \frac{L^{ref}}{t^{ref}} \mathbf{v}, & m_{\alpha} &\rightarrow m^{ref} m_{\alpha}, \\ n_{\alpha} &\rightarrow n^{ref} n_{\alpha}, & \rho &\rightarrow n^{ref} m^{ref} \rho, & n^F &\rightarrow n^{ref} e_0 n^F, & n^e &\rightarrow n^{ref} e_0 n^e, \\ \varphi &\rightarrow \frac{kT}{e_0} \varphi, \end{aligned} \quad (35)$$

where k is the Boltzmann constant. The constitutive functions and the phenomenological coefficients are substituted by

$$\begin{aligned}
\rho\psi &\rightarrow n^{ref} kT \rho\psi, & \mu_\alpha &\rightarrow \frac{kT}{m_\alpha} \mu_\alpha, & \mathbf{P} &\rightarrow \frac{kT \varepsilon_0}{e_0 L^{ref}} \mathbf{P}, \\
\mathbf{J}_\alpha &\rightarrow \frac{m_\alpha n^{ref} L^{ref}}{t^{ref}} \mathbf{J}_\alpha, & \mathbf{j}^e &\rightarrow \frac{e_0 n^{ref} L^{ref}}{t^{ref}} \mathbf{j}^e, \\
\Sigma &\rightarrow n^{ref} kT \Sigma, & \boldsymbol{\sigma} &\rightarrow n^{ref} kT \boldsymbol{\sigma}, & p &\rightarrow n^{ref} kT p, \\
\eta &\rightarrow n^{ref} kT t^{ref} \eta, & \nu &\rightarrow n^{ref} kT t^{ref} \nu, \\
M_{\alpha\beta} &\rightarrow \frac{(L^{ref})^2 n^{ref}}{t^{ref}} \frac{m_\alpha m_\beta}{kT} M_{\alpha\beta}, & R_0^i &\rightarrow \frac{n^{ref}}{t^{ref}} R_0^i.
\end{aligned} \tag{36}$$

The scaling generates a dimensionless number λ in the equations,

$$\lambda = \sqrt{\frac{\varepsilon_0 kT}{e_0^2 n^{ref} (L^{ref})^2}}. \tag{37}$$

The length λL^{ref} is related to the well known Debye length which controls the width of the boundary layers as it is indicated by Figure 1.

On the interface S we introduce a characteristic surface number density n_s^{ref} and substitute:

$$\begin{aligned}
\mathbf{w} &\rightarrow \frac{L^{ref}}{t^{ref}} \mathbf{w}, & n_s &\rightarrow n_s^{ref} n_s, \\
\rho_s &\rightarrow m_s^{ref} n_s^{ref} \rho_s, & n_s^{F/P} &\rightarrow e_0 n_s^{ref} n_s^{F/P}, \\
\rho_s \psi_s &\rightarrow kT n_s^{ref} \rho_s \psi_s, & \mu_\alpha &\rightarrow \frac{kT}{m_\alpha} \mu_\alpha, & \boldsymbol{\sigma}_s &\rightarrow kT n_s^{ref} \boldsymbol{\sigma}_s, \\
R_0^i &\rightarrow \frac{n_s^{ref} L^{ref}}{t^{ref}} R_0^i, & M_s^{\pm} &\rightarrow \frac{m_\alpha m_\beta n_s^{ref} L^{ref}}{k t^{ref}} M_s^{\pm}, & L_s^\pm &\rightarrow \frac{k t^{ref}}{m_0 m_s^{ref} n_s^{ref} L^{ref}} L_s^\pm.
\end{aligned} \tag{38}$$

The scaling of the surface equations generates a further dimensionless number

$$\delta = \frac{n_s^{ref}}{n^{ref} L^{ref}}. \tag{39}$$

Different scaling for metals Recall that we have scaled the free energy of the electrolyte by the thermal energy $E_{th} = kT$. However, for metals the Fermi-energy is the more appropriate scaling quantity. It reads

$$E_f := \left(\frac{3}{8\pi} n_M^{ref} \right)^{2/3} \frac{h^2}{2m_e}. \tag{40}$$

Here n_M^{ref} denotes the number density of metal ions and h is the Planck constant. Instead of (37), in the equations we get the dimensionless number

$$\lambda_M = \sqrt{\frac{\varepsilon_0 E_f}{e_0^2 n_M^{ref} (L^{ref})^2}}. \quad (41)$$

Discussion of the dimensionless numbers Let us consider a metal-electrolyte interface at room temperature $T = 298.15$ K. The characteristic number densities for metals n_M^{ref} and for the surfaces n_s^{ref} are given by typical spacing of the crystal lattice. For the electrolyte we assume a number density n^{ref} which corresponds to a 0.1 molar aqueous solution.

$$n^{ref} = 6.022 \cdot 10^{25} \text{ m}^{-3}, \quad n_M^{ref} = 5.86 \cdot 10^{28} \text{ m}^{-3}, \quad n_s^{ref} = 7.3 \cdot 10^{18} \text{ m}^{-2}. \quad (42)$$

Given a characteristic length of the macroscopic system

$$L^{ref} = 10^{-2} \text{ m} \quad (43)$$

we get the dimensionless numbers

$$\lambda \approx 1.54 \cdot 10^{-8}, \quad \lambda_M \approx 2.25 \cdot 10^{-7} \quad \text{and} \quad \delta \approx 1.21 \cdot 10^{-5}. \quad (44)$$

We note that the dimensionless numbers λ , λ_M and δ are very small.

In the asymptotic analysis we want to have only one single small parameter. Therefore we have to relate the numbers (44) to each other. The numbers λ and λ_M are of the same size and there is no need to distinguish between the metal and electrolyte. Instead, we can use the same scaling in both cases. Further we relate δ to λ by the substitution

$$\delta \rightarrow \delta \lambda, \quad (45)$$

such that now δ is assumed to be of order $\mathcal{O}(1)$.

In addition to this dimensionless numbers, there are several material dependent coefficients appearing in the constitutive equation (25). These coefficients have a strong influence on the dynamic behavior of the system. In liquid electrolytes, the diffusion coefficients, the viscosity coefficients and the reaction rates are of the order [Lid05]

$$\frac{kT M_{\alpha\beta}}{(m^{ref})^2 n^{ref}} \approx 10^{-9} \frac{\text{m}^2}{\text{s}}, \quad \eta, \nu \approx 10^{-3} \frac{\text{kg}}{\text{ms}}, \quad R_0 \approx 10^{23} \frac{1}{\text{m}^3 \text{s}} \quad \text{and} \quad R_s \approx 10^{21} \frac{1}{\text{m}^2 \text{s}}. \quad (46)$$

The characteristic particle mass is in the order of

$$m^{ref} = 10^{-27} \text{ kg}. \quad (47)$$

Let us consider an electrochemical system of macroscopic dimensions where the global state changes only moderately fast in time. We choose

$$t^{ref} = 10 \text{ s}. \quad (48)$$

Then the scaling (36) leads to the corresponding dimensionless coefficients

$$M_{\alpha\beta} = 10^{-4}, \quad \eta, \nu = 10^{-10}, \quad R_0 = 10^{-2} \quad \text{and} \quad R_s = 1.6 \cdot 10^{-2}. \quad (49)$$

Compared to the diffusion coefficients and the reaction rates, the values of the viscosities are very small. We conclude that viscosity has only minor influence and can be neglected. Therefore we set

$$\eta = \nu = 0. \quad (50)$$

3.2 Summary of complete model equations in dimensionless form

From now on we study for simplicity the one-dimensional version of the model. We agree that space dependent functions exclusively depend on the coordinate $x_1 = x$ which is normal to the interface S . The dimensionless version of the model from Section 2 reads as follows. In the subdomains Ω^\pm we have

$$\partial_t n_\alpha + \partial_x (n_\alpha v + J_\alpha) = \sum_{i=1}^M \gamma_\alpha^i R^i \quad \alpha = 1, \dots, N, \quad (51a)$$

$$\partial_t \rho + \partial_x (\rho v) = 0, \quad (51b)$$

$$\partial_x \Sigma = 0, \quad (51c)$$

$$-\lambda^2 (1 + \chi) \partial_{xx} \varphi = n^F. \quad (51d)$$

The constitutive equations read in dimensionless form

$$J_\alpha = - \sum_{\beta=1}^N M_{\alpha\beta} \partial_x \left(\mu_\beta - \frac{m_\beta}{m_0} \mu_0 + \left(z_\beta - z_0 \frac{m_\beta}{m_0} \right) \varphi \right), \quad (52a)$$

$$R^i = R_0^i \left[\exp \left(-\beta^i A^i \sum_{\alpha=0}^N \gamma_\alpha^i \mu_\alpha \right) - \exp \left((1 - \beta^i) A^i \sum_{\alpha=0}^N \gamma_\alpha^i \mu_\alpha \right) \right], \quad (52b)$$

$$\Sigma = -p + \lambda^2 \frac{1}{2} (1 + \chi) (\partial_x \varphi)^2 \quad \text{with} \quad p = -\rho \hat{\psi} + \sum_{\alpha=0}^N n_\alpha \mu_\alpha. \quad (52c)$$

The dimensionless jump conditions on the interface S are represented by

$$\lambda \delta \partial_t n_\alpha + \llbracket n_\alpha (v - w) \nu + J_\alpha \nu \rrbracket = \sum_{i=1}^{M_S} \gamma_\alpha^i R_s^i \quad \alpha = 1, \dots, N_S, \quad (53a)$$

$$\lambda \delta \partial_t \rho + \llbracket \rho (v - w) \nu \rrbracket = 0, \quad (53b)$$

$$\llbracket \Sigma \rrbracket = 0, \quad (53c)$$

$$-\llbracket \lambda (1 + \chi) \partial_x \varphi \nu \rrbracket = \delta n_s^F. \quad (53d)$$

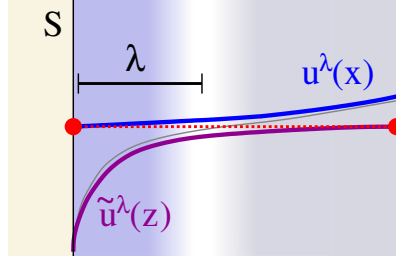


Figure 2: Formal asymptotic approach: matching of the inner approximation $\tilde{u}^\lambda(z)$ for $z \rightarrow \infty$ with the outer approximation $u^\lambda(x)$ for $x \rightarrow x_S$.

Finally, the dimensionless constitutive equations for the surface quantities read

$$\varphi = \varphi|_S^\pm, \quad (54a)$$

$$R_s^i = R_s^i \left[\exp \left(-\beta_s^i A_s^i \sum_{\alpha=0}^{N_S} \gamma_{\alpha s} \mu_{\alpha s} \right) - \exp \left((1 - \beta_s^i) A_s^i \sum_{\alpha=0}^{N_S} \gamma_{\alpha s} \mu_{\alpha s} \right) \right], \quad (54b)$$

$$(\rho_\alpha(v - w) + J_\alpha)|_S^\pm = \mp \sum_{\beta=1}^{N_S} M_{\alpha\beta}^\pm \left(\mu_\beta|_S^\pm - \mu_0|_S^\pm - (\mu_\beta - \mu_0) \right), \quad (54c)$$

$$\pm L_s^\pm (\rho(v - w))|_S^\pm = \mu_0|_S^\pm - \mu_0, \quad (54d)$$

$$\sigma = \rho\psi - \sum_{\alpha=0}^{N_S} \rho_{\alpha s} \mu_{\alpha s}. \quad (54e)$$

4 Formal asymptotic analysis

It is well known that the adjacent regions of an interface between two different electrochemical mixtures form thin layers, where the electric potential and the number densities exhibit variations with steep gradients. The method of formal asymptotic analysis is well established in electrochemistry to analyze the boundary layers at an interface, see e.g. [New65, BBC05]. As we already know from [DGM13], the relevant parameter to control the layer thickness is λ . The main idea to study the limit $\lambda \rightarrow 0$ by means of the formal asymptotic analysis is to assume for a generic function u the existence of two different expansions. An *outer expansion* u^λ is assumed to be a good approximation of u in the bulk of the domain without the boundary layers. For the *inner expansion* \tilde{u}^λ that approximates u inside the boundary layer, a rescaled space variable is used that is related to the width λ of the layer. Then the expansions are inserted into the equations and terms related to the same powers of λ are connected with matching conditions. A detailed description of the method of asymptotic analysis can be found in [CF88]. Within this section we assume for simplicity of notation that the surface normal is oriented in positive x_1 direction, i.e. $\nu = 1$.

Expansions of outer and inner solutions In the previous section the solutions of (51)-(54) are denoted by φ , n_α , v , x_S and n_s^α , suppressing the dependency on λ . Similarly we use here the generic variable u to represent any of these solutions. Within the boundary layers we introduce a new coordinate z and inner variable \tilde{u} by defining for $x \in \Omega^\pm$

$$z = \frac{x - x_S}{\lambda}, \quad \tilde{u}(t, z) = u(t, x_S + \lambda z). \quad (55)$$

We assume that in the bulk regions of Ω^\pm we have an expansion of u into a power series with respect to λ , i.e.

$$u^\lambda(t, x) = u^{(0)}(t, x) + u^{(1)}(t, x)\lambda + \mathcal{O}(\lambda^2). \quad (56a)$$

In addition we assume the existence of a second expansion that approximates \tilde{u} in the layers, i.e.

$$\tilde{u}^\lambda(t, z) = \tilde{u}^{(0)}(t, z) + \tilde{u}^{(1)}(t, z)\lambda + \mathcal{O}(\lambda^2). \quad (56b)$$

Moreover we assume that also the surface densities n_α and the parametrization x_S of S can be approximated as

$$n_\alpha^\lambda = n_\alpha^{(0)} + n_\alpha^{(1)}\lambda + \mathcal{O}(\lambda^2), \quad (57a)$$

$$x_S^\lambda = x_S^{(0)} + x_S^{(1)}\lambda + \mathcal{O}(\lambda^2). \quad (57b)$$

Matching conditions The relation (55) between inner and outer solutions and the expansions implies so called matching conditions. In [CF88, Peg89] the matching conditions are introduced as asymptotic expansions that are formally achieved by inserting the corresponding expansions into the left and right hand sides of (55) and subsequent comparison of powers of λ . The result is

$$\tilde{u}^{(0)}(t, z) \xrightarrow{z \rightarrow \pm\infty} u^{(0),\pm}(t, x_S^{(0)}), \quad (58a)$$

$$\partial_z \tilde{u}^{(0)}(t, z) \xrightarrow{z \rightarrow \pm\infty} 0, \quad (58b)$$

$$\partial_{zz} \tilde{u}^{(0)}(t, z) \xrightarrow{z \rightarrow \pm\infty} 0, \quad (58c)$$

and for the terms in higher order we get

$$\tilde{u}^{(1)}(t, z) - \partial_x u^{(0),\pm}(t, x_S^{(0)})(z + x_S^{(1)}) \xrightarrow{z \rightarrow \pm\infty} u^{(1),\pm}(t, x_S^{(0)}), \quad (59a)$$

$$\partial_z \tilde{u}^{(1)}(t, z) \xrightarrow{z \rightarrow \pm\infty} \partial_x u^{(0),\pm}(t, x_S^{(0)}), \quad (59b)$$

$$\tilde{u}^{(2)}(t, z) - \partial_x u^{(1),\pm}(t, x_S^{(0)})(z + x_S^{(1)}) \xrightarrow{z \rightarrow \pm\infty} u^{(2),\pm}(t, x_S^{(0)}). \quad (59c)$$

4.1 Leading order equations and boundary conditions

Leading order bulk equations In the bulk domains Ω^\pm the leading order equations can directly be read of from (51). We have

$$\partial_t n_\alpha^{(0)} + \partial_x (n_\alpha^{(0)} v^{(0)} + J_\alpha^{(0)}) = \sum_{i=1}^M \gamma_\alpha^i R^{i,(0)} \quad \text{for } \alpha \in \{1, \dots, N\}, \quad (60a)$$

$$\partial_t \rho^{(0)} + \partial_x (\rho^{(0)} v^{(0)}) = 0, \quad (60b)$$

$$\partial_x \Sigma^{(0)} = 0, \quad (60c)$$

$$0 = n^{F,(0)}. \quad (60d)$$

The reaction rates, mass fluxes and the total stress tensor are represented in leading order by:

$$J_\alpha^{(0)} = - \sum_{\beta=1}^N M_{\alpha\beta} \partial_x \left(\left(\mu_\beta^{(0)} - \frac{m_\beta}{m_0} \mu_0^{(0)} \right) + \left(z_\beta - z_0 \frac{m_\beta}{m_0} \right) \varphi^{(0)} \right), \quad (61a)$$

$$\Sigma^{(0)} = -p^{(0)}, \quad (61b)$$

$$R^{i,(0)} = R_0^i \left[\exp \left(-\beta^i A^i \sum_{\alpha=0}^N \gamma_\alpha^i \mu_\alpha^{(0)} \right) - \exp \left((1 - \beta^i) A^i \sum_{\alpha=0}^N \gamma_\alpha^i \mu_\alpha^{(0)} \right) \right], \quad (61c)$$

for $\alpha = 1, \dots, N$ and $i = 1, \dots, M$.

Leading order equation in the layers and jump conditions The leading order variables in the layers are $\tilde{\varphi}^{(0)}$, $\tilde{v}^{(0)}$ and $\tilde{n}_\alpha^{(0)}$ for $\alpha = 0, \dots, N$. We use the asymptotic expansions (56b) and (57) and transform (51) to the inner coordinate (55). In the leading order we obtain for $z \in (-\infty, 0)$ and for $z \in (0, \infty)$

$$\partial_z \tilde{J}_\alpha^{(-1)} = 0 \quad \alpha = 0, \dots, N, \quad (62a)$$

$$\partial_z (\tilde{\rho}^{(0)} (\tilde{v}^{(0)} - w^{(0)})) = 0, \quad (62b)$$

$$\partial_z \tilde{\Sigma}^{(0)} = 0, \quad (62c)$$

$$-(1 + \chi) \partial_{zz} \tilde{\varphi}^{(0)} = \tilde{n}^{F,(0)}, \quad (62d)$$

with the corresponding constitutive laws

$$\tilde{J}_\alpha^{(-1)} = - \sum_{\beta=1}^N M_{\alpha\beta} \partial_z \left(\left(\tilde{\mu}_\beta^{(0)} - \frac{m_\beta}{m_0} \tilde{\mu}_0^{(0)} \right) + \left(z_\beta - z_0 \frac{m_\beta}{m_0} \right) \tilde{\varphi}^{(0)} \right), \quad (63a)$$

$$\tilde{\Sigma}^{(0)} = -\tilde{p}^{(0)} + \frac{(1 + \chi)}{2} (\partial_z \tilde{\varphi}^{(0)})^2. \quad (63b)$$

At the interface for $z \rightarrow 0$ we have to transform the jump conditions (53) to the inner variables and deduce in the leading order:

$$\llbracket \tilde{J}_\alpha^{(-1)} \rrbracket = 0 \quad \alpha = 0, \dots, N, \quad (64a)$$

$$\llbracket \tilde{\rho}^{(0)}(\tilde{v}^{(0)} - w^{(0)}) \rrbracket = 0, \quad (64b)$$

$$\llbracket \tilde{\Sigma}^{(0)} \rrbracket = 0, \quad (64c)$$

$$-\llbracket (1 + \chi)\partial_z \tilde{\varphi}^{(0)} \rrbracket = \delta n_s^{F,(0)}. \quad (64d)$$

Note, that due to the coordinate transformation (55) the double brackets for an generic function \tilde{u} are given by

$$\llbracket \tilde{u}^{(0)} \rrbracket = \tilde{u}^{(0)}|_{z=0}^+ - \tilde{u}^{(0)}|_{z=0}^- \quad \text{with} \quad \tilde{u}^{(0)}|_{z=0}^\pm = \lim_{z \rightarrow 0^\pm} \tilde{u}^{(0)}. \quad (65)$$

The corresponding constitutive laws on the interface $S^{(0)}$ are

$$\tilde{\varphi}^{(0)}|_{z=0}^\pm = \varphi_s^{(0)}, \quad (66a)$$

$$(\tilde{\rho}_\alpha^{(0)}(\tilde{v}^{(0)} - w^{(0)}) + \tilde{J}_\alpha^{(0)})|_{z=0}^\pm = \mp \sum_{\beta=1}^N M_s^{\pm} M_{\alpha\beta}^{\pm} \left(\tilde{\mu}_\beta^{(0)}|_{z=0}^\pm - \tilde{\mu}_0^{(0)}|_{z=0}^\pm - (\mu_\beta^{(0)} - \mu_s^{(0)}) \right), \quad (66b)$$

$$\pm L_s^\pm (\tilde{\rho}^{(0)}(\tilde{v}^{(0)} - w^{(0)}))|_{z=0}^\pm = \left(\tilde{\mu}_0^{(0)}|_{z=0}^\pm - \mu_0^{(0)} \right), \quad (66c)$$

$$\sigma_s^{(0)} = \rho_s^{(0)} \psi_s^{(0)} - \sum_{\alpha=0}^{N_S} \rho_s^{(0)} \mu_s^{(0)}. \quad (66d)$$

The inner equations in higher order The relevant equations of the boundary layers result from the equations (51) in the inner coordinate (55), we obtain

$$\partial_z (\tilde{n}_\alpha^{(0)}(\tilde{v}^{(0)} - w^{(0)}) + \tilde{J}_\alpha^{(0)}) = 0 \quad \alpha = 0, \dots, N. \quad (67)$$

From the jump conditions (53) we get

$$\llbracket \tilde{n}_\alpha^{(0)}(\tilde{v}^{(0)} - w^{(0)}) + \tilde{J}_\alpha^{(0)} \rrbracket = \sum_{i=1}^{M_S} \gamma_\alpha^i R_s^{i,(0)} \quad \alpha = 1, \dots, N_S, \quad (68)$$

together with the equation for the interfacial reaction rates

$$R_s^{i,(0)} = R_s^i \left[\exp \left(-\beta^i A_s^i \sum_{\alpha=0}^{N_S} \gamma_\alpha^i \mu_s^{(0)} \right) - \exp \left((1 - \beta^i) A_s^i \sum_{\alpha=0}^{N_S} \gamma_\alpha^i \mu_s^{(0)} \right) \right]. \quad (69)$$

4.2 New representation of the jump conditions

The objective of this section is to reformulate the interface conditions (64), (66) and (68) in terms of the bulk quantities instead of the inner quantities $\tilde{u}^{(0)}|_{z=0}^{\pm}$. Then, we can divide the leading order equations above into two distinct sets of equations that are only weakly coupled: one set containing the leading order variables in the bulk and on the surface and the other determining the leading order variables in the layers. As a result we can formulate two new models that are summarized in Section 5.

To emphasize the differences between the original model and the leading order approximations, we denote the interface in the thin double layer limit $\lambda \rightarrow 0$ by $I = \{x_S^{(0)}\}$ and introduce new jump brackets. We define for a generic function $u^{(0)}$ on the regions Ω^{\pm}

$$u^{(0)}|_I^{\pm} = \lim_{x \rightarrow I^{\pm}} u^{(0)} \quad \text{and} \quad \llbracket u^{(0)} \rrbracket = u^{(0)}|_I^+ - u^{(0)}|_I^-. \quad (70)$$

As before, we agree that if the function $u^{(0)}$ is only defined either in Ω^+ or in Ω^- , we set the corresponding value in (70)₂ to zero. The interpretation of the new jump bracket $\llbracket u^{(0)} \rrbracket$ is, that these brackets express the jump of a quantity u across a thin double layer while the original bracket $\llbracket u \rrbracket$ is a jump across the actual interface S as illustrated in Figure 1.

Constancy of the electrochemical potential At first we show that the electrochemical potentials $\mu_{\alpha} + z_{\alpha}\varphi$ are constant in the boundary layer. Inserting the constitutive law (63b) into (62c) and combination with (62d) yields

$$\partial_z \tilde{p}^{(0)} = (1 + \chi) \partial_{zz} \tilde{\varphi}^{(0)} \partial_z \tilde{\varphi}^{(0)} = -\tilde{n}^{F,(0)} \partial_z \tilde{\varphi}^{(0)}. \quad (71)$$

On the left hand side, we apply the Gibbs-Duhem equation (34) to obtain the important identity

$$0 = \sum_{\alpha=0}^N \tilde{n}_{\alpha}^{(0)} \partial_z \left(\tilde{\mu}_{\alpha}^{(0)} + z_{\alpha} \tilde{\varphi}^{(0)} \right). \quad (72)$$

Next the matching condition (58b) is used to derive $\tilde{J}_{\alpha}^{(-1)} \rightarrow 0$ for $z \rightarrow \pm\infty$. We conclude from (62a) that $\tilde{J}_{\alpha}^{(-1)} = 0$ for $\alpha = 0, \dots, N$ and hence with (63a) we have

$$0 = \partial_z \left(\tilde{\mu}_{\alpha}^{(0)} + z_{\alpha} \tilde{\varphi}^{(0)} \right) - \frac{m_0}{m_{\alpha}} \partial_z \left(\tilde{\mu}_0^{(0)} + z_0 \tilde{\varphi}^{(0)} \right) \quad \text{for } \alpha = 1, \dots, N. \quad (73)$$

Multiplying with $\tilde{n}_{\alpha}^{(0)}$ and summing over $\alpha = 0, \dots, N$, implies the constancy of the electrochemical potentials $\tilde{\mu}_{\alpha}^{(0)} + z_{\alpha} \tilde{\varphi}^{(0)}$ within the boundary layers, i.e.

$$\partial_z \left(\tilde{\mu}_{\alpha}^{(0)} + z_{\alpha} \tilde{\varphi}^{(0)} \right) = 0 \quad \text{for } \alpha = 0, 1, \dots, N. \quad (74)$$

Reformulation of jump conditions First we consider the total stress $\Sigma^{(0)}$. From the matching condition we get

$$\lim_{z \rightarrow \pm\infty} \tilde{\Sigma}^{(0)} = \Sigma^{(0)}|_I^{\pm}. \quad (75)$$

Due to the inner equation (62c), $\tilde{\Sigma}^{(0)}$ is constant in the layers implying $\lim_{z \rightarrow \pm\infty} \tilde{\Sigma}^{(0)} = \tilde{\Sigma}^{(0)}|_{z=0}^{\pm}$. From the jump condition (64c) follows

$$\llbracket \Sigma^{(0)} \rrbracket = 0. \quad (76)$$

In analogous way we proceed for the mass flux $\tilde{\rho}^{(0)}(\tilde{v}^{(0)} - w^{(0)})$. The matching conditions and the constancy of the mass flux in the layers imply

$$(\rho^{(0)}(v^{(0)} - w^{(0)}))|_I^{\pm} \stackrel{(58a)}{=} \lim_{z \rightarrow \pm\infty} [\tilde{\rho}^{(0)}(\tilde{v}^{(0)} - w^{(0)})] \stackrel{(62b)}{=} (\tilde{\rho}^{(0)}(\tilde{v}^{(0)} - w^{(0)}))|_{z=0}^{\pm}. \quad (77)$$

From the interface condition (64b) we get

$$\llbracket \rho^{(0)}(v^{(0)} - w^{(0)}) \rrbracket = 0. \quad (78)$$

The reformulation of the partial mass balances is more difficult. Application of the matching conditions yields after some simple but cumbersome calculations to the relation

$$(n_{\alpha}^{(0)}(v^{(0)} - w^{(0)} + J_{\alpha}^{(0)}))|_I^{\pm} = \lim_{z \rightarrow \pm\infty} (\tilde{n}_{\alpha}^{(0)}(\tilde{v}^{(0)} - w^{(0)} + \tilde{J}_{\alpha}^{(0)})). \quad (79)$$

For details we referred to [DG13, DGK14] where the necessary steps for the calculation can be found. Again, by means of the inner equation (67) we see that the fluxes $\tilde{n}_{\alpha}^{(0)}(\tilde{v}^{(0)} - w^{(0)} + \tilde{J}_{\alpha}^{(0)})$ are constant. Application of the interfacial mass balances (68) yields

$$\llbracket n_{\alpha}^{(0)}(v^{(0)} - w^{(0)} - J_{\alpha}^{(0)}) \rrbracket = \sum_{i=1}^{M_S} \gamma_s^i R_s^{i,(0)} \quad \text{for } \alpha = 1, \dots, N_S. \quad (80)$$

The constitutive laws (66b) and (66c) of the normal mass fluxes to the surface contain differences of the form $\tilde{\mu}_{\beta}^{(0)}|_{z=0}^{\pm} - \mu_{\beta}^{(0)}$. According to (74) we only know that the electrochemical potentials are constant in the layers, but not $\tilde{\mu}_{\beta}^{(0)}$. For this reason, we use the continuity of the electric potential (66a), i.e. $\varphi^{(0)} = \tilde{\varphi}^{(0)}|_{z=0}^+ = \tilde{\varphi}^{(0)}|_{z=0}^-$ to rewrite constitutive laws (66b) and (66c) in terms of the electrochemical potentials. From the matching conditions we get

$$(\mu_{\beta}^{(0)} + z_{\beta}\varphi^{(0)})|_I^{\pm} = \lim_{z \rightarrow \pm\infty} (\tilde{\mu}_{\beta}^{(0)} + z_{\beta}\tilde{\varphi}^{(0)}) = (\tilde{\mu}_{\beta}^{(0)} + z_{\beta}\tilde{\varphi}^{(0)})|_{z=0}^{\pm}. \quad (81)$$

Together with one more application of (62b) and (77) we get from (66b)

$$\begin{aligned} & \pm (\rho_{\alpha}^{(0)}(v^{(0)} - w^{(0)} + J_{\alpha}^{(0)}))|_I^{\pm} \\ &= \sum_{\beta=1}^N M_s^{\pm} M_{\alpha\beta}^{\pm} \left((\mu_{\beta}^{(0)} + z_{\beta}\varphi^{(0)}) - (\mu_0^{(0)} + z_0\varphi^{(0)}) - ((\mu_{\beta}^{(0)} + z_{\beta}\varphi^{(0)}) - (\mu_0^{(0)} + z_0\varphi^{(0)})) \right). \end{aligned} \quad (82)$$

Analogously we proceed with the constitutive law (66c) and we obtain

$$\pm L_s^{\pm} (\rho^{(0)}(v^{(0)} - w^{(0)}))|_I^{\pm} = \left((\mu_0^{(0)} + z_0\varphi^{(0)})|_I^{\pm} - (\mu_0^{(0)} + z_0\varphi^{(0)}) \right). \quad (83)$$

Finally we integrate the inner Poisson equation (62d) to replace the gradients of the electric potential $\partial_z \tilde{\varphi}|_{z=0}^{\pm}$ in the interface condition (64d) by the free charge densities \tilde{n}^F . We obtain

$$\int_{-\infty}^0 \tilde{n}^{F,(0)} dz + \delta n_s^{F,(0)} + \int_0^{+\infty} \tilde{n}^{F,(0)} dz = 0. \quad (84)$$

This equation is the only remaining coupling between the variables in the bulk and surface on the one hand and the variables in the boundary layer on the other hand.

5 Summary and discussion of the reduced models

With the asymptotic analysis of Section 4 we can derive two new models for the thin double layer limit $\lambda \rightarrow 0$. On the one hand we have the *reduced bulk model* based on the leading order bulk equations and the reformulated interface conditions. This model does not resolve the interfacial charge layers spatially but consistently incorporates all their effects into new jump conditions. Thus the new interface I covers the double layer. On the other hand there is the *boundary layer model* that is based on the inner expansions and describes in detail the profiles of the layers. Both models are only weakly coupled and with appropriate assumptions on the constitutive laws describing the material behavior, e.g. a metal electrode, it is even possible to decouple the new models effectively, c.f. the example in Sect. 6. In this section, both models are summarized using the dimensional quantities. We want to introduce them as independent models of their own and for simplicity of notation we omit the superscript index (0) indicating the origin from the leading order terms of the expansions in Section 4.

5.1 Reduced bulk model

In the thin double layer limit $\lambda \rightarrow 0$, the reduced bulk model describes the evolution of the bulk variables n_α, v and φ in the domains Ω^\pm and the surface quantities n_α, w and φ on I .

Analogously to the complete model, the material dependent properties are encoded into the free energy densities

$$\rho\psi = \rho\hat{\psi}(T, \rho_0, \rho_1, \dots, \rho_N), \quad \rho\psi_s = \rho\hat{\psi}_s(T_s, \rho_{0s}, \rho_{1s}, \dots, \rho_{Ns}). \quad (85)$$

in Ω^\pm and on I respectively. Comparing with (33), we observe that $\rho\psi$ does not depend on $\partial_x\varphi$ since the term due to polarization $\frac{1}{2}\chi\varepsilon_0|\partial_x\varphi|^2$ has vanished. As before the chemical potentials are defined as

$$\mu_\alpha = \frac{\partial\rho\psi}{\partial\rho_\alpha} \quad \text{and} \quad \mu_\alpha^s = \frac{\partial\rho\psi_s}{\partial\rho_\alpha^s}. \quad (86)$$

Bulk equations In Ω^\pm we have the mass balances, the momentum balance and the local electroneutrality condition

$$\partial_t(m_\alpha n_\alpha) + \partial_x(m_\alpha n_\alpha v + J_\alpha) = \sum_{i=1}^M \gamma_\alpha^i m_\alpha R^i \quad \text{for } \alpha = 0, \dots, N, \quad (87a)$$

$$\partial_x \Sigma = 0, \quad (87b)$$

$$n^F = 0. \quad (87c)$$

We realize that there is a significant simplification compared to the complete model, since the Poisson equation (51d) (resp. (9)) is replaced by an algebraic constraint in the limit $\lambda \rightarrow 0$. Let us stress that the potential φ is still among the unknown variables but now its determination is up to the remaining equations (87a) and (87b).

Constitutive equations in bulk For the diffusion fluxes, the stress tensor and the reaction rates we have

$$J_\alpha = - \sum_{\beta=1}^N M_{\alpha\beta} \left(\partial_x \left(\frac{\mu_\beta - \mu_0}{T} \right) + \frac{e_0}{T} \left(\frac{z_\beta}{m_\beta} - \frac{z_0}{m_0} \right) \partial_x \varphi \right), \quad \alpha = 1, \dots, N, \quad (88a)$$

$$\Sigma = -p \quad \text{with} \quad p = \rho\hat{\psi} - \sum_{\alpha=0}^N m_\alpha n_\alpha \mu_\alpha, \quad (88b)$$

$$R^i = R_0^i \left[\exp \left(-\beta^i \frac{A^i}{kT} \sum_{\alpha=0}^N \gamma_\alpha^i m_\alpha \mu_\alpha \right) - \exp \left((1-\beta^i) \frac{A^i}{kT} \sum_{\alpha=0}^N \gamma_\alpha^i m_\alpha \mu_\alpha \right) \right]. \quad (88c)$$

Compared to the complete model, only the stress tensor is changed and significantly simplified. The contribution of the Maxwell stress in (25) has vanished in the limit $\lambda \rightarrow 0$.

Interface equations In the limit $\lambda \rightarrow 0$ we obtain quasi-static mass balances at the interface. The momentum balance are formally of the same structure as in the complete model. We emphasize the different interpretation of the jump terms as the jump over the double layer by the use of the triple brackets $\llbracket \cdot \rrbracket$. We have

$$\llbracket m_\alpha n_\alpha (v-w)\nu + J_\alpha \nu \rrbracket = \sum_{i=1}^{M_S} \gamma_\alpha m_\alpha R_s^i, \quad \alpha = 0, \dots, N_S, \quad (89a)$$

$$\llbracket \Sigma \rrbracket = 0, \quad (89b)$$

$$\int_{-\infty}^0 \tilde{n}^F dx + n_s^F + \int_0^{+\infty} \tilde{n}^F dx = 0. \quad (89c)$$

As in the volume, we have an electroneutrality constraint (89c) on I that replaces the jump condition related to the Poisson equation of the complete model.

Constitutive equations for the interface For the mass fluxes and and the reaction rates on I we have

$$L_s^\pm (\rho(v-w))|_I^\pm = \mp \left(\left(\mu_0 + \frac{z_0 e_0}{m_0} \varphi \right) |_I^\pm - \left(\mu_0 + \frac{z_0 e_0}{m_0} \varphi \right) \right), \quad (90a)$$

$$\begin{aligned} (\rho_\alpha(v-w) + J_\alpha)|_I^\pm = \mp \sum_{\beta=1}^{N_S} M_{\alpha\beta}^\pm \left(\left(\left(\mu_\beta + \frac{z_\beta e_0}{m_\beta} \varphi \right) |_I^\pm - \left(\mu_0 + \frac{z_0 e_0}{m_0} \varphi \right) |_I^\pm \right) \right. \\ \left. - \left(\left(\mu_\beta + \frac{z_\beta e_0}{m_\beta} \varphi \right) - \left(\mu_0 + \frac{z_0 e_0}{m_0} \varphi \right) \right) \right), \quad (90b) \end{aligned}$$

$$R_s^i = R_0^i \left(\exp \left(-\frac{\beta^i A^i}{kT} \sum_{\alpha=0}^{N_S} \gamma_\alpha^i m_\alpha \mu_\alpha \right) - \exp \left(\frac{(1-\beta^i) A^i}{kT} \sum_{\alpha=0}^{N_S} \gamma_\alpha^i m_\alpha \mu_\alpha \right) \right). \quad (90c)$$

$$\sigma_s = \rho_s \hat{\psi} - \sum_{\alpha=0}^{N_S} \rho_\alpha \mu_\alpha. \quad (90d)$$

Comparing to the constitutive equations (30) and (31), we see that instead of the chemical potentials μ_α and μ_α the electrochemical potentials $\mu_\alpha + \frac{z_\alpha e_0}{m_\alpha} \varphi$ and $\mu_\alpha + \frac{z_\alpha e_0}{m_\alpha} \varphi$ appear.

Electrostatic potential and Butler-Volmer equations The constitutive relations (90a) and (90b) contain an explicit dependence on the electrostatic potential φ that is not among the thermodynamic variables of the complete model of Section 2. There, the electric field \mathbf{E} is the thermodynamical variable instead. One has to keep in mind that the introduction of the potential φ in (90a) and (90b) relies on the constancy of the electrochemical potentials in leading order (74), what in turn is only valid under the assumptions of Section 2.1 and the choice of the characteristic quantities in (46).

In the analogous way it is also possible to rewrite (90c) in terms of the electrochemical potential on the surface and then reformulate in terms of bulk quantities. This leads to general equations of Butler-Volmer type that relate the interfacial reaction rate to a potential difference at the interface. More precisely we see that the relevant quantity is the potential difference over the thin double layer. For a detailed derivation and analysis of general Butler-Volmer equations we refer to [DGM15].

Electric current The limit $\lambda \rightarrow 0$ essentially simplifies the balance equations (18) and (20) for the electric charges in the volume and on the interface. Due to local electroneutrality $n^e = n^F = 0$ according to (87c) and (89c), we get

$$\partial_x j^e = 0 \quad \text{and} \quad \llbracket j^e \nu \rrbracket = 0. \quad (91)$$

The electric current j^e is constant in each subvolume Ω^\pm and continuous at the interface I . Hence j^e is even a global constant in all of Ω . Moreover, the representation

$$j^e = \sum_{\alpha=0}^N \frac{z_\alpha e_0}{m_\alpha} J_\alpha \quad (92)$$

is considerably simpler than (19). The convection and polarization terms have vanished in the limit $\lambda \rightarrow 0$. Entering the constitutive equation (88a) into (92) and defining

$$\kappa = \frac{1}{T} \sum_{\alpha,\beta=1}^N \left(\frac{z_\alpha e_0}{m_\alpha} - \frac{z_0 e_0}{m_0} \right) M_{\alpha\beta} \left(\frac{z_\beta e_0}{m_\beta} - \frac{z_0 e_0}{m_0} \right) \quad \text{and} \quad M_\beta = \sum_{\alpha=1}^N \left(\frac{z_\alpha e_0}{m_\alpha} - \frac{z_0 e_0}{m_0} \right) M_{\alpha\beta}. \quad (93)$$

where the coefficient κ is called the electric conductivity, we get

$$j^e = -\kappa \partial_x \varphi - \frac{1}{T} \sum_{\beta=1}^N M_\beta \partial_x (\mu_\beta - \mu_0). \quad (94)$$

If the sum on the right hand side is small and can be neglected, we get Ohms law

$$j^e = -\kappa \partial_x \varphi \quad \text{for} \quad \left| \frac{1}{T} \sum_{\beta=1}^N M_\beta \partial_x (\mu_\beta - \mu_0) \right| \ll |\kappa \partial_x \varphi|. \quad (95)$$

5.2 Boundary layer model

The spacial distribution of number densities and the profiles of pressure and potential inside the thin boundary layers are not included in the bulk model above. Instead we derive from the leading order equations of the inner expansion the boundary layer model as an additional closed set of equations. We denote the unknown variables in the layers by \tilde{n}_α , \tilde{v} and $\tilde{\varphi}$ to distinguish them from the variables of the reduced bulk model. The necessary input values are $(n_\alpha|_I^\pm, v, \varphi|_I^\pm, n_\alpha, w, \varphi)$ that are determined by the solution of the reduced bulk model.

The material dependent properties are encoded in the free energy density and the chemical potential

$$\tilde{\rho}\tilde{\psi} = \tilde{\rho}\hat{\psi}(T, \tilde{\rho}_0, \tilde{\rho}_1, \dots, \tilde{\rho}_N) - \frac{1}{2}\chi\varepsilon_0(\partial_x\tilde{\varphi})^2 \quad \text{and} \quad \tilde{\mu}_\alpha = \frac{\partial\tilde{\rho}\tilde{\psi}}{\partial\tilde{\rho}_\alpha}. \quad (96)$$

Note that consistency with the reduced bulk model of Section 5.1 requires that the function $\hat{\psi}$ is the same like in (85). An additional free energy density for the surface is not needed here.

Equations in the layer The balance equations and the Poisson equation have to be solved in the half-spaces $\tilde{\Omega}^- = (-\infty, 0)$ and $\tilde{\Omega}^+ = (0, +\infty)$, respectively. Using the unscaled space variable x , we have

$$\partial_x(\tilde{\rho}(\tilde{v} - w)) = 0, \quad (97a)$$

$$\partial_x(\tilde{\mu}_\alpha + \frac{z_\alpha e_0}{m_\alpha}\tilde{\varphi}) = 0, \quad (97b)$$

$$\partial_x\tilde{\Sigma} = 0, \quad (97c)$$

$$-(1 + \chi)\varepsilon_0\partial_{xx}\tilde{\varphi} = \tilde{n}^F. \quad (97d)$$

Note that the Poisson equation (97d) will generate boundary layers of order $\lambda \ll 1$ but in contrast to the complete model of Section 2, there is no further length scale included in the system (97).

Constitutive equation The stress tensor in the boundary layer reads

$$\tilde{\Sigma} = -\tilde{p} + \frac{1}{2}(1 + \chi)\varepsilon_0(\partial_x\tilde{\varphi})^2, \quad \text{with } \tilde{p} = \tilde{\rho}\hat{\psi} - \sum_{\alpha=0}^N m_\alpha\tilde{n}_\alpha\tilde{\mu}_\alpha, \quad (98)$$

In contrast to the stress tensor (88b) in the reduced bulk model, the stress tensor in the layers contains the Maxwell stress that has to be counterbalanced by pressure variations of \tilde{p} .

Boundary conditions At the interface $x = 0$, the boundary condition for the Poisson equation (97d) is

$$\tilde{\varphi}|_{x=0} = \varphi. \quad (99)$$

From the matching conditions (58a) we get the asymptotic limits for $x \pm \infty$

$$\lim_{x \rightarrow \pm\infty} \tilde{n}_\alpha = n_\alpha|_I^\pm, \quad \lim_{x \rightarrow \pm\infty} \tilde{v} = v|_I^\pm, \quad \lim_{x \rightarrow \pm\infty} \tilde{\varphi} = \varphi|_I^\pm. \quad (100)$$

5.3 Discussion of the scaling

The proposed new models above should not be understood as universally applicable models for general electrochemical systems. Already the validity complete model is limited by the general assumptions of Section 2.1, i.e. if the system size is large compared to the Debye length and formation of boundary layers is fast compared to the chosen time scale. The new models are restricted further by the scaling procedure (35)–(38), the choice of characteristic quantities in (42) and (43) and the scaling assumption (45). Different scalings or combinations thereof are possible and will in general lead to alternative models. To find an appropriate scaling thus requires an intuitive feeling and much care to obtain a useful reduced model for the system at hand. For each new application it is necessary to check whether or not the chosen scaling is admissible.

In particular, the relation $\delta \sim \lambda$ according to (45) is a consequence of our choice of a characteristic surface number density, viz. $n_s^{ref} = 7.3 \cdot 10^{18} \text{m}^{-2}$, which corresponds to one atomic layer. As long as the condition $n_{\alpha}/n_s^{ref} = \mathcal{O}(1)$ holds, the new models above are valid. Alternatively, one might consider surface deposition processes where the number densities of surface constituents are in the range of $n^{ref} L^{ref}$. In that case the scaling has to be replaced by

$$n_{\alpha} \rightarrow n^{ref} L^{ref} n_{\alpha} \quad (101)$$

and instead of the dimensionless surface mass balances (53) we obtain

$$\partial_t n_{\alpha} + \llbracket n_{\alpha}(v - w)\nu + J_{\alpha}\nu \rrbracket = \sum_{i=1}^{M_S} \gamma_{\alpha}^i R_s^i \quad \alpha = 1, \dots, N_S. \quad (102)$$

Here, the surface quantities are related to the fluxes from the volume without any weighting by scaling parameters δ or λ . The asymptotic analysis then yields a reduced bulk model with the surface equations

$$\partial_t n_{\alpha} + \llbracket n_{\alpha}(v - w)\nu + J_{\alpha}\nu \rrbracket = \sum_{i=1}^{M_S} \gamma_{\alpha}^i R_s^i \quad \alpha = 1, \dots, N_S. \quad (103)$$

In contrast to the quasi-static mass balances (89a), these mass balances are formally of the same structure as in the complete model, only the jump terms have a different interpretation.

6 Application of the reduced models

In this section we show how the reduced bulk model and the layer model can be used to characterize the properties of a metal-electrolyte interface. The reduced bulk model is used to determine the coverage of the metal surface with adsorbed electrolyte constituents and the resulting surface charge. Hereafter we use the boundary layer model to illustrate the charge distribution in the double layer. Combination of these two charge contributions allows a qualitative computation of one of the most important quantity of an electrochemical interface, the differential capacity.

Let a metal electrode occupy the left half-space Ω^- . The liquid electrolyte is then located in the complementary half space Ω^+ and the normal to the interface I points into the electrolyte domain. For simplicity we assume that no chemical reactions take place on the metal-electrolyte-interface, i.e. there are no electron transfer reactions that would cause Faradayic currents. The metal electrode is modeled as a binary mixture. The two species are the immobile metal ions M with the charge $z_M e_0$ and free electrons e with $z_e = -1$. The electrolyte consists of the solvent denoted by S , anions A and cations C . Since there are no surface reactions, no additional constituent needs to be considered on I .

For further simplification we consider only quasi-static processes in the bulk. Then we may assume constant distribution of the number densities in the bulk, but not inside the layers, cf. [DGM13]. The solution of the volume equations (87) is not necessary in this case and the boundary values of the bulk variables can be considered as given quantities

$$n_M|_I^- = n_M^{ref}, \quad n_e|_I^- = z_M n_M^{ref}, \quad n_\alpha|_I^+ = \bar{n}_\alpha \quad (\alpha = A, C, S). \quad (104)$$

Here n_M^{ref} is the reference number density of the metal ions. \bar{n}_α are the average number densities in the electrolyte that have to satisfy the electroneutrality condition $n^F = 0$ according to (87c). Moreover we denote by φ^M and φ^E the prescribed (spacially constant) potential in the metal bulk and the electrolyte bulk, respectively.

Hence, in the reduced bulk model, it suffices to determine the number densities n_α and the potential φ on the interface in dependency of the bulk potential difference $U = \varphi^M - \varphi^E$. Since each constituent is only present in either Ω^+ or Ω^- the interface conditions (89a)–(89c) simplify to

$$(n_\alpha(v - w) - \frac{1}{m_\alpha} J_\alpha)|_I^- = 0, \quad \alpha = e, M_s, \quad (105a)$$

$$(n_\alpha(v - w) + \frac{1}{m_\alpha} J_\alpha)|_I^+ = 0, \quad \alpha = A_s, C_s, S_s, \quad (105b)$$

$$\llbracket p \rrbracket = 0, \quad (105c)$$

$$\int_{-\infty}^0 \tilde{n}^F dx + n_s^F + \int_0^{+\infty} \tilde{n}^F dx = 0. \quad (105d)$$

The pressure is a global constant and can be set to a reference pressure, and choosing a laboratory coordinate system the interface position can be fixed, i.e.

$$p|_I^\pm = p^{ref} \quad \text{and} \quad w = 0. \quad (106)$$

The quasi-static mass balance equations (105a) and (105b) together with $L_s^\pm = 0$ simplify the constitutive equations (90a)–(90b) to the equations

$$\mu_\alpha + \frac{z_\alpha e_0}{m_\alpha} \varphi = \left(\mu_\alpha + \frac{z_\alpha e_0}{m_\alpha} \varphi \right) |_I^-, \quad \alpha = e, M_s, \quad (107a)$$

$$\mu_\alpha + \frac{z_\alpha e_0}{m_\alpha} \varphi = \left(\mu_\alpha + \frac{z_\alpha e_0}{m_\alpha} \varphi \right) |_I^+, \quad \alpha = A_s, C_s, S_s. \quad (107b)$$

6.1 Constitutive equations

In addition to the general equations (105) and (107) the specific material properties have to be encoded into the free energy densities $\rho\psi$, $\rho\psi_s$. For simplicity we assume all constituents in the electrolyte to be of the same size, i.e. solvation effects are not considered here. Instead we refer to [DGL14a, DGL14b] where these effects are studied in detail and its crucial importance for quantitatively correct solutions is demonstrated. In the following we only specify the chemical potentials and refer to [DGM13, DGL14a, DGL14b] for the derivation of the free energy densities.

Electrolyte bulk Using the simple incompressible mixture model of [DGM13], the chemical potentials in the electrolyte are given by

$$\mu_\alpha = \mu_\alpha^{ref} + \frac{v_0^{ref}}{m_\alpha}(p - p^{ref}) + \frac{kT}{m_\alpha} \ln\left(\frac{n_\alpha}{n}\right), \quad \alpha = A, C, S, \quad (108)$$

where $n = \sum_{\alpha \in A, C, S} n_\alpha$ is the total number density and μ_α^{ref} is a constant reference value. Here, it is assumed that all electrolyte constituents have the same specific volume v_0^{ref} . We refer to [DGL14a, DGL14b] for the more general case of different specific volumes. Incompressibility is characterized by the relation

$$v_0^{ref} n = 1. \quad (109)$$

This requires to introduce the pressure p as an independent variable, for details see [DGM13, DGL14a].

Metal bulk We apply the Sommerfeld model of free electrons [Som28]. We assume that the metal ions form an incompressible crystal lattice characterized by the constant number density

$$n_M = n_M^{ref}. \quad (110)$$

Similarly to the electrolyte, we thus have to replace in set of independent variables n_M by the pressure. More precisely, the partial pressure of the metal ions p_M is the independent variable and $p = p_e + p_M$, where p_e is the partial pressure of the electrons. A detailed discussion on this topic is not of interest here and can be found in [DGL14a]. The chemical potentials are

$$\mu_e = \left(\frac{3}{8\pi}\right)^{\frac{2}{3}} \frac{h^2}{2m_e^2} n_e^{\frac{2}{3}} \quad \text{and} \quad \mu_M = \mu_M^{ref} + v_M^{ref} p_M, \quad (111)$$

where v_M^{ref} is the specific volume of the metal ions and μ_M^{ref} a reference value.

Interface We assume that the metal-electrolyte interface consists of a grid of surface metal ions where each metal ion offers one site that may be occupied by an adsorbing particle from the electrolyte. In analogy to the bulk, incompressibility of the interface is characterized by a constant number density of the metal ions, i.e.

$$n_M = n_M^{ref}, \quad (112)$$

and instead of n_M , the surface tension σ is an independent variable, cf. [DGL14a]. Under the assumption that all constituents are of the same size, each particle of the electrolyte constituents A , C and S can occupy exactly one site. Thus we are led to define the density of non-occupied sites on the surface by

$$n_V = n_M - \sum_{\alpha=A,C,S} n_\alpha. \quad (113)$$

The chemical potentials on the surface are [DGL14b]

$$\mu_e = \mu_e^{ref}, \quad (114a)$$

$$\mu_M = \mu_M^{ref} - \frac{a_M^{ref}}{m_M} \sigma + \frac{kT}{m_M} \ln \left(\frac{n_V}{n_M} \right), \quad (114b)$$

$$\mu_\alpha = \mu_\alpha^{ref} + \frac{kT}{m_\alpha} \ln \left(\frac{n_\alpha}{n_V} \right), \quad \alpha = A, C, S. \quad (114c)$$

Here, μ_α^{ref} are constant reference values for the constituents A_α , a_M^{ref} is the specific surface area of metal ions on the surface. Note that the chemical potential of the surface electrons μ_e is assumed to be a constant depending only on the electrode material and surface properties like the crystallographic orientation.

Decoupling of models By the above choice of the constitutive laws, i.e. the assumption of constant chemical potential of electrons on the surface, the reduced bulk model effectively decouples from the boundary layer model. The coupling is exclusively established by (105d). At the same time (105d) remains the only equation of the reduced bulk model that depends on the number density n_e of the electrons on the surface. That means (105a)–(105c), (107a) and (107b) can be solved independently of (105d) and the equations of the boundary layer model.

6.2 The metal-electrolyte-double-layer

Here we study the behavior the metal-electrolyte-double-layer in the setting of the boundary layer model (105)–(107) with the constitutive equations for the chemical potentials above. We consider the potentiostatic case where the potential difference $U = \varphi^M - \varphi^E$ is controlled. In the following calculations we use $T = 298.15$ K and $p^{ref} = 10^5$ Pa. We use reference values to represent a (110) face of a silver electrode, viz.

$$z_M = 1, \quad n_M^{ref} = 5.86 \cdot 10^{28} \text{ m}^{-3}, \quad (115)$$

$$n_M^{ref} = \frac{\sqrt{2}}{5^{\frac{2}{3}}} (n_M^{ref})^{\frac{2}{3}}, \quad \mu_e^{ref} = 4.5071 \text{ eV}, \quad (116)$$

where the value of μ_e^{ref} is motivated by the work function for the surface. The aqueous binary electrolyte is represented by

$$z_A = -1, \quad z_C = 1, \quad z_S = 0, \quad v_0^{ref} = 3 \cdot 10^{-29} \text{ m}^3, \quad (117)$$

The reference values μ_α^{ref} and μ_α^s for the chemical potentials are given by $\Delta g_\alpha = m_\alpha(\mu_\alpha^{ref} - \mu_\alpha^s)$. For the the example at hand we use

$$\Delta g_A = 0.02 \text{ eV} , \quad \Delta g_C = -1.5 \text{ eV} , \quad \Delta g_S = 0.03 \text{ eV} . \quad (118)$$

By this choice the anions can be adsorbed to the metal surface whereas the cations are effectively not adsorbed.

Surface electric potential Electroneutrality in the bulk (104), viz. $n_e|_I^- = z_M n_M^{ref}$, and the constitutive function (111) imply the constancy of the chemical potential of the free electrons

$$\mu_e|_I^- = \left(\frac{3}{8\pi}\right)^{\frac{2}{3}} \frac{\hbar^2}{2m_e^2} \left(z_M n_M^{ref}\right)^{\frac{2}{3}} \approx 5.5037 \text{ eV} . \quad (119)$$

Since $\mu_e = \mu_e^s$ according to (107a), the potential difference between the metal bulk and the interface is also a constant, i.e.

$$U_0 = \varphi^M - \varphi_s = \frac{m_e}{e_0} \left(\mu_e|_I^- - \mu_e^s\right) \approx 1.3637 \text{ V} . \quad (120)$$

Surface coverage To relate the number densities n_α to the number of available sites on the grid of metal ions, we define the coverage

$$\theta_\alpha = \frac{n_\alpha}{n_M} , \quad \alpha = A, C, S, V . \quad (121)$$

We use the constitutive functions (108) and (114c) to obtain from (107b) a representation of the coverages as

$$\theta_\alpha = \theta_V \left(\frac{n_\alpha|_I^+}{n}\right) \exp\left(\frac{1}{kT}\Delta g_\alpha + \frac{v_0^{ref}}{kT}(p|_I^+ - p^{ref}) + \frac{z_\alpha e_0}{kT}(\varphi^E - \varphi_s)\right) , \quad \alpha = A, C, S . \quad (122)$$

Due to the definition (113) we have $\sum_{\alpha=A,C,S,V} \theta_\alpha = 1$ and deduce

$$\theta_V = \left[1 + \sum_{\alpha=A,C,S} \left(\left(\frac{n_\alpha|_I^+}{n}\right) \exp\left(\frac{1}{kT}\Delta g_\alpha + \frac{v_0^{ref}}{kT}(p|_I^+ - p^{ref}) + \frac{z_\alpha e_0}{kT}(\varphi^E - \varphi_s)\right)\right)\right]^{-1} . \quad (123)$$

Since $\varphi^E - \varphi_s = U_0 - U$, we get from (122) explicit formulas for the coverage as functions of the potential difference U , the bulk number densities $n_\alpha|_I^+$ and the pressure $p|_I^+$. In Figure 3 we see that the surface coverage of anions is a monotone increasing function of U , whereas cations are not adsorbed and hence $\theta_C \approx 0$. Moreover, increasing the electrolyte concentration, the anions start adsorbing at lower applied voltages and the coverage reaches the saturation at $\theta_A = 1$ more early when increasing U . At low applied voltages, only solvent molecules are adsorbed with $\theta_S \approx 3/4$ leaving non-occupied sites with $\theta_V \approx 1/4$. When increasing U , anions adsorb to the surface leading to $\theta_V = 0$ and replace the solvent molecules such that also $\theta_S = 0$ for large U .

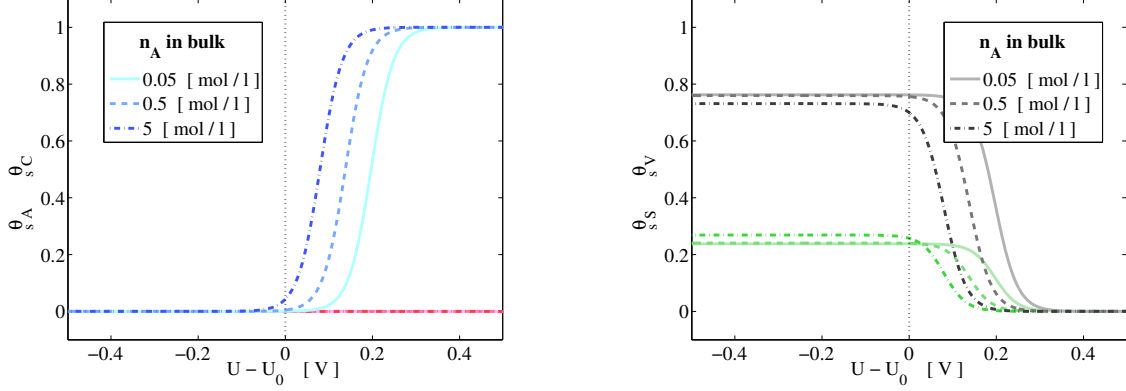


Figure 3: Surface coverage $0 \leq \theta_\alpha \leq 1$ over the applied voltage for different electrolyte concentrations. Left: anions (blue) and cations (red). Right: solvent (gray) and non-occupied sites (green).

6.3 Application of the boundary layer model

Chemical potentials in the layers In our boundary layer model, the chemical potentials are the same functions as in the bulk. We have

$$\tilde{\mu}_e = \left(\frac{3}{8\pi} \right)^{\frac{2}{3}} \frac{h^2}{2m_e^2} \tilde{n}_e^{\frac{2}{3}}, \quad (124a)$$

$$\tilde{\mu}_M = \mu_M^{ref} + v_M^{ref} \tilde{p}_M, \quad (124b)$$

$$\tilde{\mu}_\alpha = \mu_\alpha^{ref} + \frac{v_0^{ref}}{m_\alpha} (\tilde{p} - p^{ref}) + \frac{kT}{m_\alpha} \ln \left(\frac{\tilde{n}_\alpha}{\tilde{n}} \right), \quad \alpha = A, C, S. \quad (124c)$$

Due to the incompressibility assumption, we have $\tilde{n}_M = n_M^{ref}$ in the metal and $v_0^{ref} \tilde{n} = 1$ in the electrolyte and the pressure \tilde{p} and \tilde{p}_M in the electrolyte and in the metal, respectively, takes the role of an independent variable.

Model equations Given the surface potential φ computed from the reduced bulk model, we can also compute the spacial distribution of number densities and the potential in the thin double layer by using the boundary layer model (97a)–(97d). With the boundary conditions

$$\lim_{x \rightarrow -\infty} \tilde{n}_e = z_M n_M^{ref}, \quad \lim_{x \rightarrow -\infty} \tilde{\varphi} = \varphi^M, \quad (125a)$$

$$\lim_{x \rightarrow +\infty} \tilde{n}_\alpha = \bar{n}_\alpha, \quad \lim_{x \rightarrow +\infty} \tilde{\varphi} = \varphi^E, \quad (125b)$$

$$\lim_{x \rightarrow \pm\infty} \tilde{p} = p^{ref}, \quad \lim_{x \rightarrow 0^\pm} \tilde{\varphi} = \varphi, \quad (125c)$$

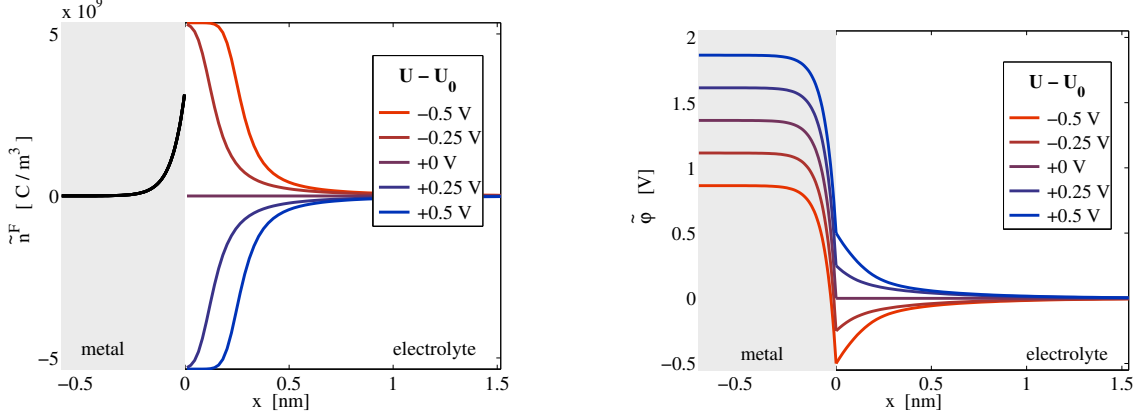


Figure 4: Charge distribution and electrostatic potential for an electrolyte with 0.5 mol/l anions for different applied voltages. Left: charge distribution in the double layer. Right: spatial profile of the potential.

we can derive from (97) and (107) the representation formulas

$$\tilde{n}_\alpha = n_\alpha|_I^+ \exp \left(\frac{v_0^{ref}}{kT} (p|_I^+ - \tilde{p}) + z_\alpha \frac{e_0}{kT} (\varphi^E - \tilde{\varphi}) \right), \quad (126a)$$

$$\tilde{n}_e = z_M n_M^{ref} \left(\frac{m_e}{E_f} \mu_e|_I - \frac{e_0}{E_f} (\varphi^M - \tilde{\varphi}) \right)^{\frac{3}{2}}. \quad (126b)$$

Then it remains to solve the nonlinear coupled system

$$-(1 + \chi) \varepsilon_0 \partial_{xx} \tilde{\varphi} = \tilde{n}^F, \quad (127a)$$

$$\partial_x \tilde{p} = -\tilde{n}^F \partial_x \tilde{\varphi} \quad (127b)$$

in Ω^- and in Ω^+ , respectively, with the corresponding boundary conditions from (125).

Numerical simulation For the numerical simulation we approximate the domains Ω^\pm by $\Omega_h^- = (-20\lambda_M, 0)$ and $\Omega_h^+ = (0, 40\lambda)$. Then piecewise linear finite elements are used for the discretization and the resulting system is solved by Newton's method. In the electrolyte we set $\chi = 80$ and in the metal $\chi = 0$.

Figure 4 shows the profile of the electrostatic potential across the metal-electrolyte-interface for different applied voltages. Due to the constant chemical potential of the surface electrons according to (114a), the profile of the electron density n_e and hence also n^F is independent of the applied external voltage. As a consequence we also observe that the profile of $\tilde{\varphi}$ in the metal is always the same, up to a shift depending on U . In particular, the voltage $U_0 = \varphi^M - \varphi^s$ between the metal bulk and the metal surface is constant. On the electrolyte side we can see, that for positive applied voltages $U - U_0$ the anions accumulate in front of the interface whereas for negative voltages $U - U_0$ cations accumulate. If $U = U_0$, there is no space charge layer in the electrolyte. An important feature of the model is that the local number densities, and hence the charge, stay bounded when voltages far from U_0 are applied. The reason for this saturation

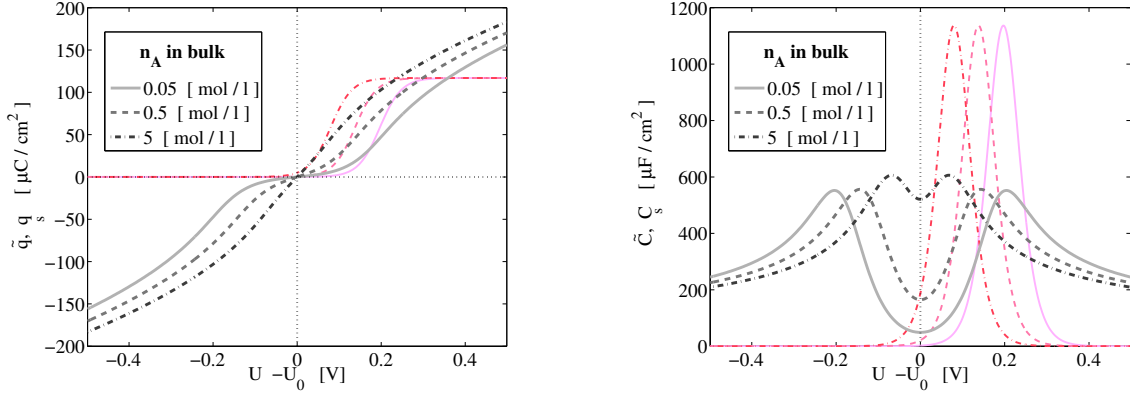


Figure 5: Left: charge \tilde{q} in the boundary layer (gray) and surface charge q (red curves) over applied voltage for different electrolyte concentrations. Right: gray curves show \tilde{C} and red curves are C .

is the coupling of the Poisson equation (127a) and the momentum balance equation (127b). For better quantitative results, the incorporation of solvated ions is most important, cf. [DGL14a]

6.4 Electric charge and differential capacity

Electric charge Application of an external voltage leads to a redistribution of charge in the double layer. There are two contributions to the charge of the electrolyte. Besides a charge \tilde{q} stored in the boundary layer we also have to account for a surface charge q of the electrolyte constituents. We define the surface charge of the electrode [NTA04]

$$q = - \sum_{\alpha=A,C,S} z_{\alpha} e_0 n_{\alpha} = - \sum_{\alpha=A,C,S} z_{\alpha} e_0 \theta_{\alpha} n_M, \quad (128a)$$

$$\tilde{q} = - \int_{\Omega^+} \tilde{n}^F dx = - \sum_{\alpha=A,C,S} z_{\alpha} e_0 \int_0^{+\infty} \tilde{n}_{\alpha} dx, \quad (128b)$$

$$Q = q + \tilde{q}. \quad (128c)$$

Using the representation formulas (126), the boundary layer charge \tilde{q} can be computed from the numerical solution of (127). Both charge contributions q and \tilde{q} are monotone functions of the applied voltage U that vanish for $U = U_0$. While \tilde{q} attains negative values for $U < U_0$, q is non-negative and bounded from above, see Figure 5.

Differential capacitance From the representation formulas (122) and (126) for the surface coverage and the number densities in the layers, respectively, we deduce that both q and \tilde{q} are in general functions of the potential difference U , the surface metal density n_M , the electrolyte

densities $n_\alpha|_I^+$ and the pressure $p|_I^+$. Since $p|_I^+ = p^{ref}$ and $n_M = n_M^{ref}$ according to (112) and (106), respectively, the remaining dependencies are

$$q = \hat{q}(U, n_\alpha|_I^+) \quad \text{and} \quad \tilde{q} = \hat{q}(U, n_\alpha|_I^+). \quad (129)$$

Changing the applied voltage in a quasi-static way, the assumption (104) is still valid, i.e. $n_\alpha|_I^+ = \bar{n}_\alpha$. The derivative of Q with respect to U is known as the differential capacity C of the surface,

$$C(U, n_\alpha|_I) = C_s(U, n_\alpha|_I^+) + \tilde{C}(U, n_\alpha|_I^+) = \frac{\partial \hat{q}(U, n_\alpha|_I^+)}{\partial U} + \frac{\partial \tilde{q}(U, n_\alpha|_I^+)}{\partial U}. \quad (130)$$

In Figure 6, the differential capacity C of the double layer is plotted. Comparing with experimental measurements [Val81, Val82, Val89], we first observe that the computed values are too large by order of magnitude. This had to be expected in advance because the effect of solvated ions is neglected here, see also [DGL14a]. In [DGL14b] it is shown that the complete model yields quantitative agreement with the measurements when solvated ions are taken into account. Nevertheless, there is qualitative agreement with the experimental curves of [Val81, Val82, Val89]. The differential capacity has a local minimum at U_0 and two local maxima of different height, where the distance between the maxima increases with the concentration of the electrolyte. For more concentrated electrolytes, the height of the maxima slightly increases.

In Figure 5 we see that the boundary layer capacity \tilde{C} is symmetric around U_0 , where \tilde{C} has a local minimum. In addition, each curve has two distinct local maxima before they decay for large deviations from U_0 . This agrees with the results of [Val81, Val82, Val89] in the case of an electrolyte that does not adsorb to the electrode surface.

Moreover, we see from Figure 5 that the surface contribution C_s has only one local maximum because only the anions adsorb to the surface. For large applied voltages, C_s vanishes because once the surface is completely occupied by anions, no additional charge can be stored. For small U , no charged electrolyte constituents adsorb to the surface at all, leading to $q = 0$ as well as $C_s = 0$.

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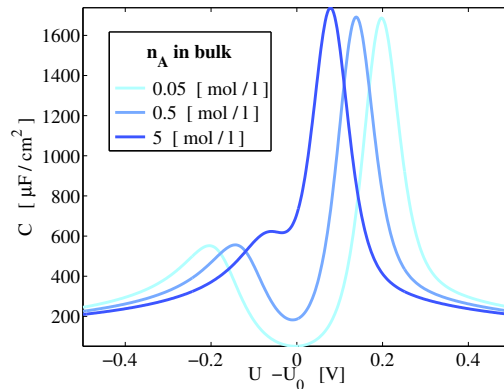


Figure 6: Differential capacity C of the double layer over applied voltage for different concentration of the electrolyte.

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