



Theory and structure of the metal–electrolyte interface incorporating adsorption and solvation effects



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ABSTRACT

In this work we present a continuum theory for the metal–electrolyte interface which explicitly takes into account adsorption and partial solvation on the metal surface. It is based on a general theory of coupled thermo-electrodynamics for volumes and surfaces, utilized here in equilibrium and a 1D approximation. We provide explicit free energy models for the metal and electrolyte phases and derive a surface free energy for the species present on the metal surface. This surface mixture theory explicitly takes into account the very different amount of sites an adsorbate requires, originating from solvation effects on the surface. Additionally we account for electron transfer reactions on the surface and the associated stripping of the solvation shell. Based on our surface free energy we thus provide explicit expressions of the surface chemical potentials of all constituents. The equilibrium representations of the coverages and the electric charge are briefly summarized. Our model is then applied to three representative examples and compared to experimental data. The Ag(110)|KPF₆ example serves to discuss some general aspects of our model and validate our theory when no specific adsorption of ionic species occurs. Next, the Ag|NaClO₄ interface for (110), (100), and (111) metal surfaces compares our theory to multiple experimental data and shows its validity within the experimental error. Finally we discuss the structure of the Ag(110)|NaF interface in a wide potential range. It turns out that various layers self-consistently form within the overall space charge region, which are compared to historic and recent pictures of the double layer. Based on this we present new interpretations of what is known as inner and outer Helmholtz-planes and finally provide a thermodynamic consistent picture of the metal–electrolyte interface structure.

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1. Introduction

One of the main questions of modern electrochemistry is certainly *how* the structure of the metal–electrolyte interface actually looks like for externally applied potentials. This question has a long history in physical chemistry, and many conceptual suggestions of the double layer structure have been proposed. The most common view *a priori* sketches the formation of several layers in front of the metal surface, namely the inner Helmholtz-plane, which covers specifically adsorbed ions, the outer Helmholtz-plane, covering *non-specifically adsorbed* ions and the diffuse double layer (c.f. Fig. 1).

This conception of the double layer structure was *transferred* to theoretical models, in order to understand various phenomena

occurring at electrochemical interfaces. The groundbreaking observations by Lippmann [2] and Gouy [3] of the electro-capillarity lead to the development of the double layer theory by Helmholtz, Chapman [4], Stern [5] and others at the beginning of the 20th century. The theory was developed further by numerous researches [6–8] and found its preliminary completion in 1947 with the seminal paper of D. Grahame [9]. The theory used by Grahame relies on Gibbsian thermodynamics for the surface, the theory of O. Stern for non-specifically adsorbed ions, and statistical mechanics (Boltzmann distribution or Gouy–Chapman theory) in order to determine the diffuse part of the double layer.

Common to all of these modeling approaches is the translation of an *a priori perception* of the double layer to a mathematical model. Based on these models the crucial quantity characterizing the metal–electrolyte interface was computed: the differential capacitance. Although the theory of Grahame describes qualitatively several aspects of the measured capacitance, its agreement is restricted to a rather narrow potential range, i.e. ± 0.1 V, as well as small salt concentrations. Especially the diffuse layer part, i.e. the Gouy–Chapman theory, is restricted to several mV around

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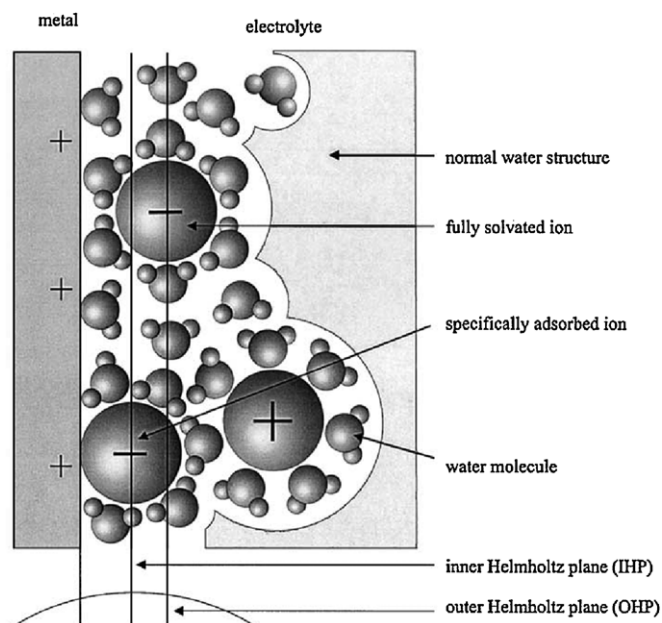


Fig. 1. Sketch of the metal–electrolyte interface structure according to D. Kolb (Fig. 1.a from [1], reprinted with permission from Elsevier)

the potential of zero charge and marked as “brilliant failure” [10] by Bockris. Several extensions of Grahame’s theory have been proposed, e.g. concentration dependent susceptibilities [11,12], hard-sphere interactions [13], steric effects [14,15], in order to overcome this problem. However, there is no satisfactory agreement of the differential capacitance with respect to potential and salt concentration.

The question is, if the approach of an *a priori perception*, and its translation to a mathematical model, is at all constructive. It seems rather *impossible* to extend Grahame’s treatment systematically to curved surfaces, various metals, higher concentrations, mixtures of electrolytes, different solvents and so on. Its consistent embedding in non-equilibrium thermodynamics is outstanding and may even be impossible. However, this step is crucial for many disciplines adjacent to fundamental electrochemistry, i.e. corrosion and colloidal science, battery and fuel cell research, porous material science, etc.

With this work we provide a conceptionally different strategy. We do not prescribe at all any structure of the metal–electrolyte interface, but rather compute it based on coupled continuum thermo-electrodynamics for volumes [16,17] and surfaces [18,19]. The continuum approach ignores some atomistic fluctuations of the material, but covers many aspects of its microscopic structure in the central quantity of continuum thermodynamics: the free energy density. Rational thermodynamics states some general, material independent conditions and reduces the whole *material modeling* to the derivation of an explicit free energy function. This strict separation between general conditions, which hold for every material, and material specific free energy densities allows for a systematic modeling of the metal, its surface, and the electrolyte within one general theory. Of course, many atomistic and even quantum chemical methods [20] are used nowadays to study the behavior and the structure of the metal–electrolyte interface. And in fact, these models are superior if one is interested in calculating microscopic phenomena like solvent orientation or density oscillation near the surface [21]. But these approaches often lack a relationship to macroscopic, measurable quantities, which is our aim here. Nevertheless continuum thermodynamics relies on certain material parameters, like the solvation number, which cannot be derived

within the framework itself. These have to be either determined from an independent experiment, or from some microscopic theory. In the view of multi-scale modeling it is hence highly desirable to have valid connection between microscopic models which determine the material parameters and their impact on measurable quantities based on continuum thermodynamics.

The metal is described by metal ions and free electrons in the conduction band, whereas the electrolyte consists of neutral solvent, several ionic as well as undissociated species. Particularly we consider all species additionally on the surface in terms of a surface mixture theory. We provide explicit functions of the free energy for all phases, which account for solvation effects in the volume and on the surface, incompressibility, entropic contributions and reference states. The electrostatic potential arises naturally within the theory due to the consistent derivation based on non-equilibrium thermo-electrodynamics. We emphasize that an *a priori* distinction between Galvani or Volta potentials is not necessary. We are then able to deduce representations of the double layer charge Q and the capacitance C based on our model. The remaining set of parameter are well defined equilibrium properties and discussed within this work.

Fig. 2 displays a comparison between computed and measured capacitance curves for aqueous NaF solutions in contact to Ag(110). We obtain a broad qualitative and quantitative agreement to the experimental data and emphasize that all parameters are kept fixed, except the bulk salt concentration. This remarkable accordance is achieved by a consistent incorporation of the material pressure p within the electrolyte in our derivation, which is completely neglected in Grahame’s theory. However, the pressure term actually accounts for the very different sizes (partial molar volumes) of solvent and solvated ions and is thus the main contribution which encodes the solvation effect. Particularly within the boundary layer the pressure p adopts very high values, which are counter balanced by the Maxwell stress, and thus cannot be ignored. It turns out that the free charge density n^F is not a function of the electric potential φ alone, which is common to all continuum double layer theories, but subject to the coupled problem

$$\nabla p = -n^F(\varphi, p)\nabla\varphi, \quad -\varepsilon\Delta\varphi = n^F(\varphi, p). \quad (1)$$

A similar relationship is also found on the surface which couples the surface charge density to the surface tension.

The comparison in Fig. 2 validates our theory in the potential range of $E = [-1.3, -0.5]$ V. We are thus able to compute of the corresponding double layer structure based on the equation system (1). Fig. 3 displays exemplarily the computed structure for $E = -0.6$ V, which corresponds to a metal surface/electrolyte potential drop of $\varphi - \varphi^E = 0.37$ V. The space dependent mole densities of solvent, cations and anions are the solid lines whereas the respective coverages on the metal surface are encoded in the bar chart. The electrostatic potential is shown as black dashed line.

We find indeed the formation of several layers in front of the metal surface. Based on the classical perception, we reinterpret our findings in the terminology of inner- and outer Helmholtz plane, Stern layer, diffuse layer, and provide sharp definitions. However, very significant differences are found to some classical assumptions, e.g. that of a constant Stern layer width or a *fixed* layer of adsorbates forming the inner Helmholtz plane. We discuss this more in detail in Section 11.

This work should be understood as general thermodynamic framework for arbitrary metal–electrolyte interfaces. Some selected examples serve to show its validity. However, we derive the whole equation system universal enough to account for mixtures of salts, weak acids, different solvents, electron transfer reactions, metal surface orientations and other effects. It allows further for a systematic extension to non-equilibrium situations,

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