FEATURE ARTICLE

Double layer theory

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The double layer is the heart of electrochemistry: All electrochemical reactions occur in this region, and it determines one of the basic macroscopic relations of electrochemistry, that between the electrode charge and the potential, or equivalently its interfacial capacitance. But even after more than a century of investigations, there is no theory, model, or simulation, from which we can calculate the capacitance of a simple system like the interface between a planar Ag(111) electrode and a 1 M solution of $HClO_4$. There are two aspects to consider: the microscopic structure, and the macroscopic relation between charge and potential. Concerning the latter, we understand this in two limiting cases: (1) for semiconductor electrodes, where it is governed by the space charge layer in the semiconductor and (2) for dilute electrolytes, where it is governed by the space charge layer in the solution as described by Gouy-Chapman theory. Needless to say, the interesting case is the interface between a conductor and a fairly concentrated electrolyte, where both sides contribute equally.

As far as the microscopic structure is concerned, this has been explored in the last decades mainly by molecular dynamics simulations, either based on classical force fields [1] or, more recently, based on density functional theory (DFT) [2]. The former use models that are well-tested in the bulk of electrolyte solutions; the electronic response of the electrode surface is usually neglected. The latter suffer from the disadvantages of DFT simulations: small ensemble size, short times for statistical sampling, and the uncertainties of DFT such as the charge delocalization error [3]. Having watched so-called ab initio simulations from the sidelines, I was bemused how the prescriptions to treat water by DFT changed over time.

Nevertheless, there are a few things which we have learnt:

There is an extended boundary layer at the interface, where particle densities and the electrostatic potential oscillate. The water bilayer, known from water adsorption on metals in ultrahigh vacuum, is not stable in electrochemical systems at ambient temperatures.

Simple geometrical models based on concepts like the inner or outer Helmholtz plane or the Stern layer have no scientific basis. They should be buried in the cemetery of discarded electrochemical concepts with the hydrogen in status nascendi.

The concept of an effective dielectric constant which varies rapidly in the boundary layer is ill-defined. Of course, it can be used for fitting results, but this does not give any scientific insights.

The approach of an ion towards an electrode surface is governed by a competition between the chemical or physical forces of the electrode and the change in solvation. The resulting balance depends on all parts of the system, e.g., in aqueous solutions, small univalent cations like Li^+ or Ag^+ can approach a metal surface while keeping the major part of their solvation energy, while desolvation makes the approach of larger or multivalent ions difficult [4].

It is impossible to construct an analytical or semi-analytical double layer theory; attempts like the various forms of modified Poisson-Boltzmann theories [5] have given some insights into the deficiencies of the simple theory, but not led to any quantitative results.

At the moment, most approaches start with a DFT-based model for the electrode, which is complemented by a simple model for the solution, such as a version of the modified Poisson-Boltzmann theory [6] or a classical DFT model for the electrolyte [7]. They have the advantage that the whole system is modeled, so that the electrode potential can be defined and its effect on the interface be explored in a consistent, but not necessarily realistic manner. Their main drawback is that they treat the two adjoining phases in a grossly unequal manner: the electrode in atomic details, the solution by simple continuum models, which had proved to be inadequate in the

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1970s. I once tried to model silver deposition, one of the fastest electrochemical reactions, with an implicit solvent and had to conclude, that the energy of activation was high and the reaction extremely slow.

Before looking into the future let us draw some inspiration from the past. In the 1980s, a major advance was achieved in double layer theory by combining two conceptually simple models: an ensemble of hard sphere ions and dipoles for the solution, and the jellium model for metals [8]. Both models are atomistic and their combination explained the dependence of the capacitance on the nature of the metal, and introduced such important concepts as oscillations in the potential and the particle densities in the boundary layer of the solution, and the response of the metal electrons to the changes in the double-layer field. While this model was far from perfect, it was the first to treat both the solution and the electrode on the same level.

Similarly, future models have to treat electrode and the electrolyte on the same atomic level. So the answer cannot be DFT plus a primitive model of the electrolyte. A step in the right direction is DFT plus RISM [9] (reference interaction site model)—the latter is a method to treat simple molecular models of an electrolyte by integral equation techniques. However, since all interactions are averaged radially, I doubt that this will be able to describe the path of a particle from the bulk to the surface and its subsequent reaction. But perhaps it can give reasonable values for the capacity.

An obvious possibility is QM/MM, but this has the problem of how to connect the quantum-mechanical and the molecular mechanical parts. In addition, the two parts have to be constantly adapted if we want to follow the path of a particle. So far I have witnessed a few attempts, but none of them convincing.

Perhaps we have fallen victims to the lures of DFT? The various packages that are on the market are easy to learn, and they give seemingly exact results for the ground states of metal surfaces with adsorbates, and have been very useful in this respect. But let us not forget that it is based on approximations of unknown quality to an unknown functional, and has therefore a semi-empirical component. Experts in DFT know which flavor to use under what circumstances, which gives DFT a touch of a craft.

Since DFT is not exact in any case, and has its limitations in system size, in the treatment ions, and in the definition of the electrode potential, why not look for semi-empirical methods which can treat larger systems comprising both the electrode and the solutions, and whose parameters can be obtained from DFT? An example: The embedded atom method [10] has been quite useful in studying the stability and the formation of surface structures on metal electrodes [11]. If this could be combined with a molecular model for metal ions in the solution, we could understand the details of metal deposition. If we could add the electronic response of the metal, we could obtain the capacitance. So let us look beyond DFT, and use our scientific imagination! There is no easy answer—otherwise I would not be writing this article, but working at it.

Finally, during the last decade, electrochemists have started to work with nanotubes and pores. This has opened a new area of the double layer in confined spaces [12], which offers new challenges beyond the reach of conventional theory.

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