

Computer Simulations of Electrochemical Systems

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We review briefly the developments and the actual state of the art in the field of molecular level simulations of the electrochemical interface between aqueous ionic solutions and simple metals.

Key words: molecular simulation, interaction model, electrochemical interface, ionic hydration, diffuse layer

1 Introduction

Electrolyte solutions have been among the first chemical systems extensively studied at the molecular level by computer simulations. Bulk aqueous alkali-halide and alkaline-earth halide solutions have thus been investigated under very different conditions of concentration, temperature, and density both by Monte Carlo (MC) and Molecular Dynamics (MD); this field has been reviewed [1]. Interaction models based on effective pair-potentials and/or potentials derived from ab-initio quantum-chemical calculations have been used to describe the intermolecular interactions. Later on, investigations have been extended to more complex ions, other solvents, and also to ionic solutions in mixed solvents [2–5]. More recently, simulation methods have been employed to investigate non-homogeneous systems such as interfaces between aqueous ionic solutions in the vicinity of the liquid/gas interface and near structureless or structured walls [6–9], metals [10–17,19–22], or model membranes [23–30]. The electrochemical aspects of this work have been reviewed recently [31–34]. Improved interaction models, for example including three-body interactions [35,36], or treating the molecular polarizabilities explicitly [37,48,39–47], are also continuously being put forward.

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Schematically, one can distinguish two main directions in present day research in the field of molecular modeling and simulations. In the first instance, one attempts to treat more and more complex systems using relatively simple and standardized interaction models. Commercial software packages are sometimes used here. In the second instance, it is mainly the aim to achieve a more fundamental understanding of the inter- and intramolecular interaction mechanisms and their consequences for the structure and the dynamics in condensed phases and to investigate new physical phenomena, not accessible through the more conventional methods. A prominent example of this approach is the ongoing effort to model 'acidity' and proton transfer (see e.g. [49]).

The lecture presented at the 7th International Fischer Symposium by one of us (PB) attempted to give a brief review of a few of the main ideas and developments in as far as they are relevant to electrochemistry, and more particularly to the understanding of the "electrochemical interface" between ionic solutions, mostly aqueous, and metals. First, a few of the many modeling strategies are briefly characterized and simulation results concerning the structure and the dynamics of aqueous salt solutions are recalled. Solid/liquid interfacial systems are in the focus of the following part. In this particularly active field of research, a rich body of results has been elaborated recently, and a few characteristic examples will be discussed. Remarks concerning the analytical and predictive power of computer simulations as well as an outlook to future applications are then offered as a conclusion.

2 Bulk Electrolyte Solutions

Water is the dominant species in electrolyte solutions. A reliable and computationally efficient description of its intermolecular interactions is thus paramount for any modeling effort in this field. Since, however, there is (still?) no universal model capable of describing accurately the complex structural, thermodynamic, and dynamic behavior of liquid water, (not to mention the various modifications of ice, or the supercritical fluid), a suitable model must be selected as a function of the type of system and the observables to be studied.

The simplest 'rigid' models, mostly used in molecular simulations of aqueous systems, describe the H₂O molecule as a rigid body with proper mass and moments of inertia. The intermolecular interactions are expressed as sums of site-site pairwise additive potentials; each of these potential terms consisting usually of an electrostatic term between partial charges located at the various sites on the molecular frame, plus other, empirical, terms, very often of Lennard-Jones (12-6) type. The distribution of the partial charges is often chosen such as to lead to a molecular dipole moment of $\mu_{\text{H}_2\text{O}}=2.1\text{-}2.4$ D, larger than the gas phase value of 1.86 D, thus taking into account, in an average fashion, the polarization of a molecule by its neighbors in the bulk. Such models are thus often termed 'effective potentials'.

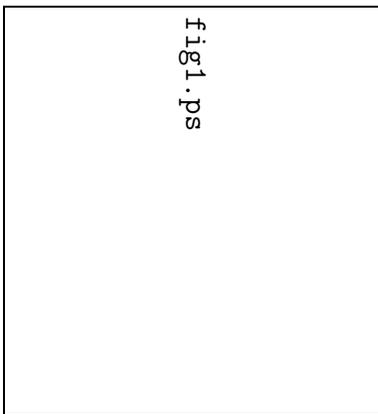


Fig. 1. The three radial distribution functions (RDF) for pure water, from simulations at room temperature and experimental density [55] with the BJH-model [51] (dashed lines), and from neutron scattering experiments [56,57] (full lines). From bottom to top: $g_{OO}(r)$, $g_{OH}(r)$, and $g_{HH}(r)$. The intermolecular peaks in $g_{OH}(r)$ and $g_{HH}(r)$ are shown for the simulation results. These peaks were removed from the experimental data before extracting the intermolecular contributions.

It is also possible to model the intramolecular degrees of freedom of the water molecule [50,51]. In this case the total interaction energy is written as a sum of atom-atom pairwise additive intermolecular terms, similar to the ones described above, and intramolecular ones. These so-called flexible models allow for some molecular polarization through the deformation of the molecule, e.g. the lengthening of the intramolecular O-H bonds. They are, however, more demanding than the 'rigid' ones in terms of computer time. The explicit treatment of the instantaneous polarization of the molecules in the simulation is the next step in increasing the sophistication of the molecular description [37].

Ab-initio quantum-chemical calculations are more and more used to guide the elaboration of all these types of interaction models. Ultimately, one would, of course, wish to dispense completely with the notion of 'models' and compute directly from first principles the interactions during the simulation. First steps in this direction for aqueous systems have been reported recently [52–54]. The computational effort, however, to study such systems is still prohibitive except for small systems (say less than 100 particles) over quite short times (say less than 10 ps).

The solute-solvent and solvent-solvent interaction models are presently mostly derived from quantum-chemical calculations through fitting procedures. It has been shown that the pair-potential approach is no longer reasonable for ion-water interactions with small and highly charged cations, where higher terms are necessary [35]. Similar procedures are often used for the more complex case of the interactions with surfaces; we shall come back to this point in sections III and IV.

Figure 1 shows, as an example, the three atom-atom radial distribution functions (RDF) for water at room temperature, computed from extensive molecular dynamics (MD) simulations [55] and neutron scattering [56,57]. This kind of agreement between experiment and simulation is achieved with several of the usually employed water models; note also

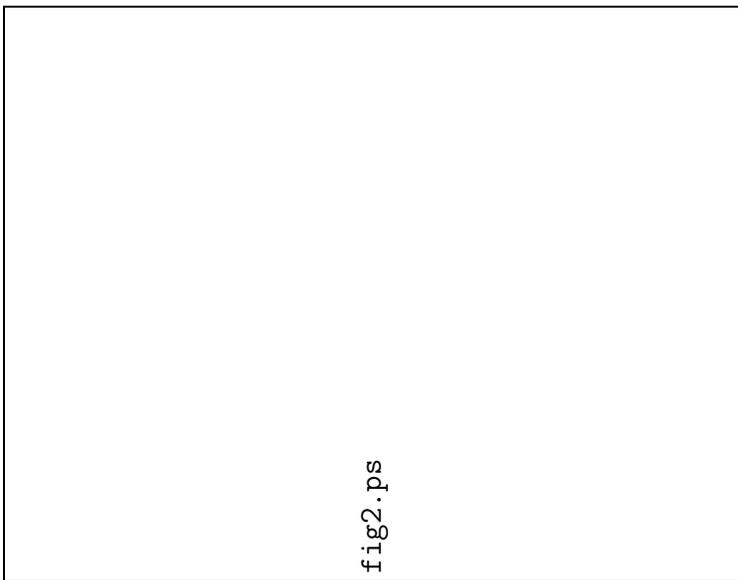


Fig. 2. Ion-water radial distribution functions ($g_{\text{Ion-O}}(r)$, solid lines, and $g_{\text{Ion-H}}(r)$, dashed lines) and corresponding running integration numbers $n(r)$ for 2.2 molal alkali halide solutions.

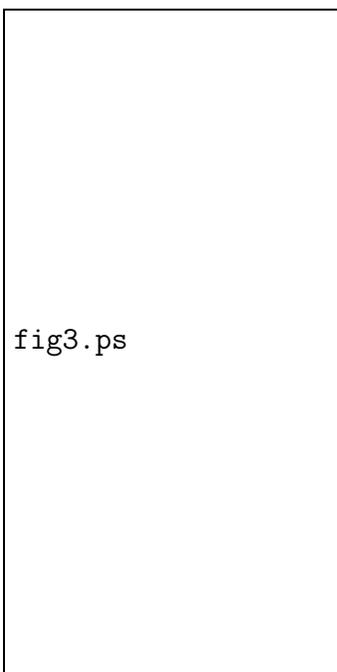


Fig. 3. Cation-water radial distribution functions ($g_{\text{Ion-O}}(r)$, solid lines, and $g_{\text{Ion-H}}(r)$, dashed lines) and corresponding running integration numbers $n(r)$ for 1.1 molal alkaline earth chloride solutions.

that uncertainties remain with respect to the experimental results, particularly the exact heights of the peaks [58].

Figures 2, 3, and 4 show typical ion-water RDF's from aqueous alkali halide and alkaline earth chloride solutions at moderate concentrations (1 to 2 molal) at room temperature.



fig4.ps

Fig. 4. Be^{2+} -water radial distribution functions ($g_{\text{Be}^{2+}-\text{O}}(r)$ and $g_{\text{Be}^{2+}-\text{H}}(r)$, solid lines) and corresponding running integration numbers $n(r)$ (dashed lines) for a 1.1 molal BeCl_2 solution, from a simulation with three-body ion-water interactions [35].

The positions of the first peaks agree quite satisfactorily with available experimental data from x-ray and neutron scattering [1], the heights of the peaks increase with increasing ionic charge and decreasing ionic radii. The integral over the first peak is usually defined as the hydration number of the ion; it is seen that for large and weakly charged ions such a definition may not be without ambiguity. The relative positions of the ion-oxygen and ion-hydrogen peaks reflect the orientation of the water molecules in the hydration shells.

This is not the place to discuss the finer details of ionic solvation as determined from simulations and experiments. These systems have been studied with many simulation methods and models, and a consistent picture has emerged, although ambiguities may remain as far as certain details are concerned. The limits of the pair-potential ansatz have been demonstrated in the case of the hydration of the Be^{2+} [35] and Al^{3+} -ions [59,60]. For the present purpose, we can say that this body of work provides a solid basis for studies of the more complex interfacial systems.

3 Simple Interfacial Systems

Besides work on the free surface [61–64], the first interfacial systems to be investigated by computer simulations were liquid-solid interfaces, where the solid was represented by a structureless (uncorrugated) wall, usually modeled by a simple repulsive potential, or by a Lennard-Jones potential [66,67]. These studies were quickly extended to ionic solutions [68], generating thus a first highly simplified model of the electrochemical interface.

Figure 5 shows, as an example from such work [69], the influence of a structureless (9-3) LJ wall on the local oxygen and hydrogen densities as a function of the distance z from the surface. These density profiles, here normalized to the bulk density of oxygen, are the one-dimensional analogues to the more familiar RDF. It is obvious that the perturbations are small and extend over approximately 10 Å into the liquid; this extension of the perturbation is also found if dynamical quantities, e.g. the self-diffusion, is studied. An only slightly larger depth of surface-induced inhomogeneities has been found for the



fig5.ps

Fig. 5. Oxygen (full line) and hydrogen (dashed line) density profiles (normalized to the bulk density of oxygen) for water near a (9-3) Lennard-Jones wall.

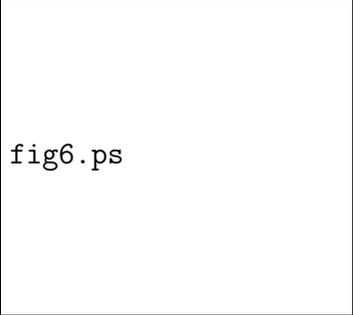


fig6.ps

Fig. 6. Oxygen density profiles from simulations of water near a rigid mercury (111) surface in a homogeneous external electric field. The surface charge density (in units of $\mu\text{C cm}^{-2}$) is indicated. The curves are shifted for better visibility.

perturbed layer near two-dimensional arrangements of charged carboxylic head-groups [70,71]. Indeed, liquids confined in pores of such, or slightly larger, dimensions may exhibit a behavior very peculiar in many respects. These systems are the focus of ongoing research [72], but we shall not deal with this aspect here.

4 The Electrochemical Interface

Building on the knowledge and experience accumulated from the work on aqueous solutions and simple interfaces, simulations evolved towards a realistic representation of the interactions between the electrode and the aqueous solution. The following model features are of paramount importance: The surface corrugation experienced by solute and solvent molecules, the anisotropy of the molecule-surface interactions, and the representation of the metallic character of the surface. Furthermore, for certain metals, e.g. mercury, the mobility of the metal atoms is non-negligible.

One of the most important aspects in electrochemical modeling is the investigation of the interfacial properties as a function of applied external potential or surface charge density on the electrode. Figure 6 shows the oxygen density profile from a series of Molecular Dynamics (MD) simulations of pure water near mercury surfaces at various surface charge densities. To keep the model simple, the mercury surface was kept rigid.

fig7.ps

Fig. 7. Average value of the difference between the z -value of a Li^+ (I^-) ion and the z -values of the mercury atoms in the first layer, from a simulation of hydrated ions near a mobile mercury surface, see text.

Interaction potentials based on extensive ab-initio calculations of molecules on top of metal clusters by Nazmutdinov *et al.* [73] were used here for the interactions between water and the mercury surface. Even at the highest surface charge densities in Fig. 6 no perfect ordering occurs. At vanishing surface charge densities, the preferred configurations are oxygen-down configurations.

A shift of the first maximum of the oxygen density is observed in Fig. 6, in analogy to the X-ray reflectivity experiments by Toney *et al.* [74]. At positive surface charges, the oxygen atoms are located closer to the surface and the hydrogen atoms (not shown) are further away. This means that, upon variation of the surface charge density from negative to positive values, the preferential orientations of water change from configurations where one or two hydrogen atoms point toward the surface to such ones where the oxygen atom is closer to the surface. However, contrary to the (currently very controversial) experiments, which show a drastic increase in water density, the simulation results show a slight overall density decrease in the first layer at very large surface charge density. The discrepancies have prompted further work on this problem [75].

Figure 7 shows, as a further example, a result obtained from MD simulations of the details of the structure and dynamics of water and hydrated ions near a liquid mercury surface [76]. Here, the mobility of the mercury atoms in the liquid was taken into account; a mercury-mercury interaction potential was developed for this purpose [77]. In keeping with this, ion-mercury- [78], water-mercury- [73], and ion-water- (see first reference in [10]) potentials derived from quantum-mechanical calculations were used, and the water-water interactions were described by the flexible BJH model [51]. Since the surface is not assumed to be rigid, there will not only be an influence of the metal onto the liquid, but, vice-versa, the aqueous solution will also influence the metal. This is seen in Fig. 7: It shows the average value of the difference, $\Delta z(\rho)$, between the value of z , the coordinate perpendicular to the surface, – surface being determined by the average over the instantaneous positions of the Hg-atoms –, for an ion and that of a mercury atom in the surface layer, for a given value of ρ , where ρ is the projection of the distance vector between the ion and the mercury atom onto the xy -plane: $\Delta z(\rho) = \langle z_{\text{ion}} - z_{\text{Hg}}(\rho) \rangle$.

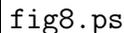
A rectangular box with a thin black border. Inside the box, the text "fig8.ps" is centered in a plain, black, sans-serif font.

Fig. 8. Density profiles and running integrals of the ion densities in 2.2 molal NaCl solutions for Na^+ (full lines) and Cl^- (dashed lines) at three different surface charge densities, as indicated. The top frame shows the oxygen atom density profile as a reference.

The distances $\Delta z(\rho)$ for large values of ρ have the highest weight and, therefore, represent the average distance of the ion from the surface, about 3.3 Å and 2.8 Å for Li^+ and I^- , respectively. For small values of ρ the Δz -values are about 2.8 and 3.7 Å. This means that the Hg-atoms near the I^- are pushed back from the surface significantly and the second nearest neighbors pulled out, forming an environment like a small impact crater. In contrast, the first as well as the second nearest Hg-atoms near a Li^+ are somewhat pulled out, forming a small hill on the surface. From this and other evidence, both structural and dynamical, it has been concluded that a lithium-ion in the interfacial layer is mostly controlled by the ion-water interactions, while for I^- , the metal-ion interactions dominate over the weak ion-water ones. In this sense, I^- is contact adsorbed on the liquid mercury surface while Li^+ is not.

While single ion studies can provide very detailed information, it is presently not possible to grasp in this way the entire complexity of the electrochemical interface, and simplifications must be introduced. For instance, Figure 8 shows some recent results of simulations of a 2.2 molal NaCl solution in contact with charged and uncharged model electrodes. The metal is modeled by a corrugated Morse potential in conjunction with the image charge model [79]. This model is more primitive than in the case of the studies of water and single ions near mercury surfaces, but it renders possible simulation times of several nanoseconds, which are necessary in order to achieve statistically meaningful results in this case. The model deliberately relinquishes specific ion-metal interactions in order to investigate solely the role of ion hydration in the double layer. Thus, both ions interact with the surface in an identical manner.

In the simulations on which Fig. 8 is based, the excess surface charge is compensated by an excess of counter ions in the liquid phase. The density profiles of cations and anions are oscillatory in nature, contrary to the simple picture of the Gouy-Chapman theory, which yields monotonous ion density profiles (but is, strictly speaking, invalid at the high

ion density). Near the uncharged electrode, the adsorption maxima are small; the cation density is significantly higher than the anion density. From the figure, and also from other studies, it is manifest that small cations like Na^+ and Li^+ can get very close to the interface, since they can form a rather stable hydration shell while located between the first and second water layer. This is not possible for the larger anions. At the positive surface charge density, the Cl^- anions become contact adsorbed, while the Na^+ ions form a layer of counter-charge between the first and second water layer at the corresponding negative surface charge density. The different behavior of the ions is a consequence of the differences in hydration energy; the balance between hydration energy and electrostatic attraction to the surface keeps the cations solvated, while in the case of the anions, the surface attraction dominates over the smaller hydration energy. This is qualitatively in keeping with the findings of the abovementioned detailed study.

In analogy to the RDFs in the bulk phase, the running integral over the density in Fig. 8 yields the number of molecules between the electrode and a given distance z from the surface. The distance at which the difference between the running distance of cations and anions becomes equal to the negative surface charge (-2 , 0 , and $+2$ at $\sigma = +9.9 \mu\text{C cm}^{-2}$, $\sigma = 0 \mu\text{C cm}^{-2}$, and $\sigma = -9.9 \mu\text{C cm}^{-2}$, respectively) can be taken as a measure for the thickness of the double layer. In all cases, the double layer thickness is less than 10 \AA , and thus in the range of several Debye lengths ($r_D = 2.1 \text{ \AA}$ at the studied electrolyte concentration), suggesting that the Gouy-Chapman theory gives at least a rough estimate of double layer thickness.

5 Summary and Conclusions

Computer simulations at the molecular level have evolved to become one of the preferred approaches for investigations of the electrochemical interface. The main challenges and difficulties are to be found firstly in the problem of determining and representing the interactions between a metallic surface and the ions and molecules in the aqueous phase, and secondly in the limitations in extension and time of the systems that can be studied. Compromises are thus necessary. Sophisticated interaction models can thus be used to investigate in detail “local” properties, i.e. ones which converge rapidly in space and time. The work on the structure and dynamics of ions adsorbed near a mercury surface [76] is an example of this approach. Simplified models must be employed if properties with less favorable convergence behavior, often ones associated with species present only at low concentration in the system, are to be studied. The determination of ion density profiles [80,81] is a case in point. These studies have only recently become possible and offer a fascinating view of the properties of the diffuse layer. It is highly mobile, and the concept of ‘diffuse layer structure’ is only valid at time scales of nanoseconds or more.

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