

# Summary

This thesis consists of 18 papers, in which we investigated the behavior of molecules and ions at aqueous interfaces by means of molecular dynamics (MD) simulations.

We started our simulations with the surface of neat water, where we investigated the behavior of hydronium and hydroxide ions, i.e., the products of autolysis of water that are of  $10^{-7}$ M concentration in pure water. The results, ranging from ab initio high level calculations on water clusters and ab initio dynamics on small systems to statistically converged classical molecular dynamics simulations are mutually consistent<sup>47,48,50</sup>. The observed surface adsorption of hydronium is also consistent with the surface selective spectroscopy experiments (VSFG, SHG, PES)<sup>45,51,55</sup><sup>{59}</sup>, surface tension measurements<sup>60</sup>, and with  $\zeta$ -potential measurements of acidic solutions<sup>62,63</sup>. The spectroscopy and surface tension experiments are also in agreement with the weak surface repulsion/non-accumulation of hydroxide observed in our simulations. However, there are macroscopic measurements, such as higher pH electrophoretic mobility measurements, titration of oil emulsions, and thin  $\mu$ m stability experiments that indicate a negative charge on air/water and oil/water interfaces<sup>61</sup><sup>{71}</sup>. Even though these experiments do not directly reveal the chemical nature or position of the observed charge, the consistency among them at different conditions led the researchers to interpretation in terms of a strong adsorption of hydroxide at interfaces<sup>64</sup><sup>{66}</sup>. Therefore, more experiments and simulations, directly addressing the chemical nature and exact location of the interfacial charge, are needed to resolve the present controversy. Nevertheless, it is at least clear now that the surface of neat water is not ion free.

In the second project connected with atmospheric research we examined polycyclic and heterocyclic aromatic hydrocarbons at the water surface. This class of organic compounds is environmentally significant due to its toxicity for humans and mass production in petrol combustion and biomass burnings<sup>8,122</sup>. The free energy profiles associated with moving benzene, naphthalene, anthracene, phenanthrene, and pyridine across the air/water interface were calculated using MD simulations. A sizable surface free energy minimum corresponding to orders of magnitude surface enhancement was found for all the above species<sup>80</sup>. This, together with surface accumulation of atmospheric oxidants such as O<sub>3</sub> or OH<sub>2</sub> has important implications for chemical reactions in the troposphere, especially for regions rich in water surface such as clouds, fogs, and mists. In other words, chemistry proceeds differently in clouds than in air. Our results are in agreement with recent experiments on thin water  $\mu$ ms and atmospheric  $\mu$ eld measurements<sup>77</sup><sup>{79,81,82,123</sup><sup>{125}</sup>.

In a biochemically oriented study we investigated ion specific effects that are responsible for protein association (salting in and salting out), denaturation, and change in activity. As mentioned in the introduction, these phenomena are usually explained in terms of the Hofmeister series<sup>27,30,31,33,126</sup>, however, a molecular understanding is still missing. We have found that for cations local ion pairing with proteins surfaces plays an important role, which was further quantified by MD simulations and ab initio calculations employing a polarizable continuum model for the solvent<sup>85</sup>. Particularly, sodium has about twice higher affinity for the carboxyl group, a functional group of negatively charged amino acids, than potassium. Also, other anions were ordered according to

their preference for sodium and potassium, i.e., the two most abundant monovalent cations in biological systems<sup>87,89</sup>. Our results are in agreement with the proposed model of matching hydration free energies<sup>87,89</sup> and are supported by conductivity and activity coefficients measurements<sup>85,86</sup>. This opens a way to molecular understanding of ion specific phenomena on proteins and other biomolecules.

Cellular membranes also interact with salts in the natural environment and several ion specific phenomena were observed<sup>98,102,105,107,109,111,112,127,132</sup>. For this study we developed and tested a new all-atom force field for DOPC lipids based on the Generalized Amber force field, which is consistent with alkali halide salts parametrization<sup>118</sup>. The influence of the membrane physical properties were computed and the mechanisms of ion-lipid interactions were identified. Our results were supported by experiments using fluorescence spectroscopy<sup>119</sup>. In addition to the model of a single lipid bilayer, we investigated a multicomponent asymmetric system mimicking the plasma membrane of eukaryotic cells in a natural environment<sup>120</sup>. This represents a first step toward detailed studies of complicated biological membrane systems with atomistic resolution.

To summarize, in this thesis we demonstrated the general applicability of MD simulations for investigating aqueous interfaces. These provide us with a molecular insight into the surface phenomena and give relevant information for many different fields ranging from atmospheric chemistry, biochemistry, and biology to technology and industry.