Integral equation theory for the electrode-electrolyte interface with the central force water model. Results for an aqueous solution of sodium chloride

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Submitted to The Journal of Chemical Physics
(October 25, 2018)

Abstract

The structure of an aqueous solution of sodium chloride at a planar electrode is investigated by integral equation techniques. With the central force water model the aqueous electrolyte is modelled as a mixture of sodium and chloride ions and partially charged hydrogen and oxygen atoms interacting via effective spherically symmetric pair potentials. The correlation functions obtained from the Ornstein-Zernike equation with Reference-Hypernetted-Chain closure gives a good description of the bulk structure (e.g. hydrogen bonded water network, solvation shell). With the bulk information and the Wertheim-Lovett-Mou-Buff equation we have calculated the density profiles at the uncharged and charged electrode. The rather rigid ice-like water structure found previously at the neutral surface strongly repels the ions. Steric interactions between the differently sized ions and the ice-like water structure dominates the ionic distribution near the electrode. This model electrolyte also responds differently to opposite charges on the electrode. We found the asymmetry in the differential capacitance curve entirely determined by the response of the interfacial water structure.
I. INTRODUCTION

In a previous article [1] we have described an integral equation method for calculating accurate bulk correlation functions for the central force (CF) water model and reported results about the water structure at an electrode. The central force water model [2], which represents water as a stoichiometric mixture of partially charged hydrogen and oxygen atoms interacting via spherically symmetric pair potentials, allows a completely molecular description of water within the framework of integral equation theory. The effective pair potentials include the information about the proper triangular arrangement of atoms within the water molecule, the molecular dipole moment and the formation of hydrogen bonds. This water model has been successfully employed and optimized in computer simulations [3,4]. The water structure obtained near the electrode has been interpreted in terms of an ice-like arrangement of water molecules in good agreement with several computer simulation and integral equation results [5]. In this paper we extend our previous investigations to an aqueous model electrolyte and consider the consequences of the interfacial water structure on the structure of the electrical double layer [7].

Early theoretical investigations of the electrical double layer neglected the molecular nature of the solvent. The solvent was approximated as a dielectric continuum and solvent effects appear only in mediating the Coulombic interactions. A mean-field treatment of this primitive model electrolyte leads to the Gouy-Chapman theory for the double layer, which holds in the dilute regime where the diffuse part of the electrical double layer is dominated by the long ranged Coulomb interactions. The remaining inner layer adjacent to the electrode was assumed to be formed by solvent molecules and excluding nonspecifically adsorbed ions. Several phenomenological models for the water monolayer employing adjustable parameters for the specific water interaction with the electrode were proposed to account for the experimental data [8,9]. Of particular interest is the pronounced asymmetry of the differential capacitance with respect to the potential of zero charge, which characterizes the interface between an aqueous electrolyte and a mercury electrode [10].

A step further towards a microscopic description of the liquid side of the interface was achieved by employing integral equation methods based on the statistical mechanics of liquids [11] or on density functional arguments [12,13]. First of all, in the ’primitive model’ of an electrolyte the ions were treated as hard spheres with a point charge in the center. Then the continuum solvent was replaced by molecular models. Even for the simplest model electrolyte of equal sized hard sphere ions and dipolar hard spheres a detailed fluid structure emerges throughout the interface as a consequence of both solvent and ionic interactions [14–16]. With respect to the tetrahedral charge distribution within a water molecule, Torrie et al. supplemented the point dipole model by a quadrupole tensor of symmetry and strength appropriate to reasonably represent the water molecule. As a result of the highly orientational interactions between these water-like molecules an ice-like solvent structure is formed near a smooth, curved [8] and planar surface [17] in a region, which is usually attributed to the ’inner layer’ of the double layer structure. Adding an octupole moment to the model yields a net polarization of the interfacial solvent structure at the neutral surface [18]. In spite of some difficulty in making the electrode completely planar, the interfacial structure obtained with these multipolar water models resembles computer simulation results for more elaborate water models [8].
These more sophisticated steric water models (e.g. ST2, TIP4P and SPC) have been employed mainly in computer simulations because of their complexity. Several authors have focused their attention on how the detailed atomic structure of the electrode affects the interfacial structure of pure water for instance through chemical bonding, surface corrugation and image interactions modelling a metal electrode. The model parameters are based on quantum mechanical ab initio calculations or on thermodynamic data. Present day computer simulations are restricted, especially for an aqueous electrolyte near an electrode, to systems with only a few ions and a few hundred of water molecules representing a highly concentrated electrolyte. Serious problems arise also from limitations in computing time, because long simulation runs are necessary to observe the ions entering and leaving the interfacial region, and special molecular dynamics techniques have been applied. Therefore it is difficult to obtain statistically reliable results from computer simulations near an interface. However, computer simulations for the complex electrode-electrolyte interface are just at the beginning. Recently, first results of an X-ray diffraction experiment indicated some interesting water structure near the electrode as well.

In comparison with the simulations, integral equation methods are more versatile when considering less concentrated electrolytes or when applying an external electric field on the interfacial structure and varying the field strength. This is in particular important for calculating the differential capacitance. In this paper we use the Wertheim-Lovett-Mou-Buff (WLMB) integral equation for determining the density profiles at the uncharged and charged electrode. We take the central force model as an appropriate water model for our calculations. The most dramatic effect of the specific water structure established near a planar surface on the electrical double layer is to be expected for ions with small cationic and large anionic size. Such a candidate is sodium chloride dissolved in water, which is particularly important in many electrochemical and biological applications.

In Sec. II. the model for the aqueous solution of sodium chloride and the method for calculating bulk correlation functions is described. Results for the structure of the ionic hydration shell and for ion pairing are presented and discussed. In the first part of Sec. III. the WLMB-equation for the density profiles of a mixture of charged particles in contact with a planar electrode is given. The equation requires particle-particle correlations, which are taken from the bulk fluid. In the region near the electrode the water solvent shows the ice-like layering. We discuss the effect of the ice-like water structure on the distribution of the differently sized sodium and chloride ions. In addition, we study the influence of an external electric field on the interfacial structure and the implications on the differential capacitance. Conclusions are summarized in Sec. IV.

II. THE BULK ELECTROLYTE

A. Model and computational method. The model electrolyte used within this paper is designed to represent sodium chloride dissolved in water. As an appropriate water model for the integral equations we employ the central force (CF) water model in the revised version. The central force model describes water as a stoichiometric mixture of partially charged hydrogen and oxygen atoms ($q_H = 0.32983 \text{e}$ and $q_O = -0.65966 \text{e}$) interacting via pairwise additive central force potentials, which are designed to reproduce the formation of water
molecules and their tetrahedral coordination via hydrogen bonds. The detailed form of the pair potentials are given in reference [1]. Implicitly, the water molecules formed by the central force pair potentials are flexible. In spite of its simplicity this water model is known to yield good results for the bulk structure and for the water structure at a hard wall [1].

The interaction potential between the ion and each atom of the water molecule consists of a Lennard-Jones pair potential added to the Coulomb interaction

\[ u_{\alpha\beta}(r) = \frac{q_\alpha q_\beta}{r} + 4 \epsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^6 \right]. \] (1)

We have fitted, according to the procedure proposed by Pettitt et al. [26], the Lennard-Jones parameters to the Hartree-Fock binding energy of the ion-water dimer in the equilibrium configuration, which has been determined for some alkali- and halide-water dimers by Kistenmacher et al. [27] with quantum mechanical ab initio calculations. The Lennard-Jones parameters for the interaction between a sodium or chloride ion and the atoms of a CF-water molecule are listed in table I. This parametrization of the ion-water interaction potential is by no means unique. Another set of pair potentials for describing the interaction between a sodium or chloride ion and the CF water molecule were derived by Bopp et al. [28]. Their pair potentials are able to yield a quite satisfactory representation of the dimer energy surface obtained from the ab initio calculations over a wide range of ion-water separation. But they imply some important inconsistencies in the asymptotic behaviour of the correlation functions and as a result some thermodynamic properties, for instance the pressure calculated according to the virial equation or the isothermal compressibility, are not defined.

The pair potentials between like ions are of the Huggins-Mayer form

\[ u_{\alpha\alpha}(r) = \frac{q_\alpha^2}{r} + B_{\alpha\alpha} \exp[-r/\rho_{\alpha\alpha}] - \frac{C_{\alpha\alpha}}{r^6} \] (2)

with potential parameters taken from [26]. The interaction between the sodium and the chloride ion was modelled in addition to the Coulomb interaction by a Lennard-Jones pair potential with parameters \( \epsilon_{NaCl} = 2.816 \times 10^{-14} \text{ erg} \) and \( \sigma_{NaCl} = 3.6 \text{ Å} \) as proposed by Smith and Haymet. [29]. Taking instead the Huggins-Mayer form of reference [26] for the pair interaction between the unlike ions and considering an ion concentration of 0.01 molar, convergent solutions of the Ornstein-Zernike equation are not obtained with the iteration procedure used for calculating the bulk correlation functions. We have found that convergence is not achieved because of a thermodynamic instability of the electrolyte solution, which can be characterized as a demixing of ions and the water solvent. The demixing cannot be avoided by changing the form of the interaction potential or the approximations employed in the iteration scheme, only the onset can be shifted [30].

Since within the chosen model electrolyte the aqueous solution of sodium chloride is simply a homogeneous mixture of charged particles interacting via additional short ranged, spherically symmetric pair interactions, the Ornstein-Zernike equation for calculating the correlation functions reads

\[ h_{\alpha\beta}(r) = c_{\alpha\beta}(r) + \sum_\gamma \rho_\gamma \int d\mathbf{r}' \ h_{\alpha\gamma}(r') \ c_{\gamma\beta}(|\mathbf{r} - \mathbf{r}'|) \] (3)
together with the closure relation

$$\ln g_{\alpha\beta}(r) = -\frac{1}{k_B T} u_{\alpha\beta}(r) + h_{\alpha\beta}(r) - c_{\alpha\beta}(r) - B_{\alpha\beta}(r).$$

(4)

$k_B$ is the Boltzmann constant, $T$ is the temperature and $\rho_\gamma$ denotes the number density of particle species $\gamma$. Including the so called bridgefunction $B_{\alpha\beta}(r)$ in the closure equation (4) gives an exact relation between the pair potential $u_{\alpha\beta}$ and the pair distribution function $g_{\alpha\beta} = 1 + h_{\alpha\beta}$. These bridgefunctions are known only for simple liquids and mixtures but not for more complex fluids like water or the aqueous electrolyte. Therefore these functions have to be approximated. $B_{\alpha\beta} = 0$ is the familiar hypernetted chain (HNC) approximation. Application of the HNC-approximation for calculating the water correlation functions failed to reproduce the structural properties of pure water [31]. Previously [1], we have developed bridgefunctions for the central force water model quite similar to those proposed by Ichiye et al. [32]. Employing our bridgefunctions in the Ornstein-Zernike formalism yields a faithful description of the structural and thermodynamic properties of pure water under standard conditions. For instance two hydrogen atoms are bound to an oxygen atom forming together the triangular water molecule. Approximately two more hydrogen atoms are located near the oxygen atom at a distance, which is comparable to the hydrogen bond length indicating the formation of the hydrogen bonded water network. We have added these bridgefunctions in the closure relation (4) for the water correlations in the electrolyte, while the remaining ion-water and ion-ion correlation functions are calculated with the HNC-approximation. The set of coupled Ornstein-Zernike integral equations (3) together with the closure relations (4) are solved iteratively at fixed temperature $T$, water density and ion concentration. The results are the correlation functions $h_{\alpha\beta}(r)$ and $c_{\alpha\beta}(r)$ in the bulk electrolyte. For details of the numerical calculation the reader is refered to reference [1]. In the calculations, presented in this article, the temperature is fixed at $T = 300 K$ and the number densities for hydrogen and oxygen atoms are chosen $\rho_H = 0.06690 \text{ g/cm}^3$ respectively $\rho_O = 0.03345 \text{ g/cm}^3$ equivalent to the mass density $\rho = 1 g/cm^3$.

B. Structural results. With the integral equation method presented above we have calculated bulk correlation functions for a 0.01 molar aqueous solution of sodium chloride, which means 5555 water molecules per sodium chloride molecule. In Fig.1a and 2a the pair distribution functions $g_{\alpha\beta}(r)$ of hydrogen and oxygen atoms around a central $Na^+$- and $Cl^-$-ion, respectively, are shown. Both ion-oxygen distribution functions exhibit a sharp first maximum determining the position of water molecules in the first hydration shell around the ion. We found the first oxygen atoms at a distance $r_{NaO} = 2.34 \text{Å}$ apart from the sodium ion and at $r_{ClO} = 3.52 \text{Å}$ for the chloride ion. The positions of hydrogen and oxygen atoms in the ionic hydration shells are summarized in table II.

Due to the stronger ion-water interaction the hydration shell of the smaller sodium ion is more pronounced. The broad maximum of the function $g_{NaH}(r)$ is obviously a superposition of two separte maxima with different weight. We have fitted two gaussian functions to this part of the curve to determine the position of the two maxima. The first maximum is found at $r_{NaH} = 2.69 \text{Å}$ and the second at $r_{NaH} = 3.21 \text{Å}$. The hydrogen atoms contributing to the first hydration shell of the $Na^+$-ion are located at distances slightly smaller and larger than expected for a single water dipole perfectly aligned in the radial electric field of the
sodium ion. The arrangement of atoms described by the pair distribution functions can be interpreted as the water dipole in the \( Na^+\)-hydration shell tilted with respect to the oxygen-ion vector and one of the 'lone pair'-valencies of the water molecule is orientated towards the ion. Obviously, this orientation is energetically more favourable because one more hydrogen bond with water molecules in the second hydration shell can be established compared to the configuration where the water dipole is radially pointing away from the sodium ion and always both 'lone pair'-valencies are directed towards the ion. Due to the packing of water molecules in the first hydration shell some molecules are also tilted with respect to the plane formed by the dipole vector and the oxygen-ion position vector. This leads to the double maximum of \( g_{NaH}(r) \). In order to evaluate the mean orientation of water molecules in the cationic hydration shell and to compare with computer simulation results it is convenient to consider the angle \( \theta \) enclosed by the dipole vector of the water molecule and the oxygen-ion position vector. We deduce the mean value of \( \theta \) from the positions of the maxima of the pair distribution functions \( g_{\alpha\beta}(r) \) under the assumption that the geometry of the water molecule in the hydration shell is not strongly perturbed by the neighbouring ion. This assumption seems to be well justified by computer simulations [33]. A value of \( \theta = 100^\circ \) corresponds to the first maximum of \( g_{NaH}(r) \) and \( \theta = 145^\circ \) to the second. With the weight of the gaussian fit functions we obtain \( \theta = 117^\circ \) for the mean orientation of water molecules in the cationic hydration shell. Our results for \( \theta \) are summarized in table III together with results obtained in computer simulations. With regard to the results of Heinzinger et al. [28], \( \theta \) is obtained from their values of \( \langle \cos \theta \rangle \). The second set of values for the mean orientation is deduced from the pair distribution functions reported by Smith et al. [29]. Some uncertainties should be attributed to the results obtained from the pair distribution functions, since the angle \( \theta \) is very sensitive to the geometrical parameters of the water model and to the location of pair distribution maxima. Nethertheless, \( \theta \) calculated with the integral equation method is in fairly good agreement with the computer simulation results.

In addition we have calculated the running coordination numbers

\[
N_{\alpha\beta}(r) = 4\pi \rho_\beta \int_0^r dx x^2 g_{\alpha\beta}(x)
\]

(5)

of hydrogen and oxygen atoms around the central ion in order to characterize the hydration shell. In Fig.1b and 2b the coordination numbers are plotted as a function of distance from the center of the ion. As a consequence of the pronounced \( Na^+\)-hydration shell the function \( N_{NaO}(r) \) possesses a well defined plateau. The coordination numbers, listed in table IV, are defined as the value of \( N_{\alpha\beta}(r) \) at the first minimum of \( g_{\alpha\beta}(r) \). Around the \( Na^+\)-ion we found on average 6.5 oxygen atoms. In our calculation the ratio \( N_{NaH}/N_{NaO} \) of the coordination numbers according to the first minima of the pair distribution functions is 2.28, quite similar to a simulation result [33], indicating that also hydrogen atoms of the second hydration shell contribute to the first \( g_{NaH}(r) \)-maximum.

In a dilute solution the energy of ionic solvation consists of two parts: the solvent re-organization energy due to the creation of a polarized cavity in the pure solvent and the interaction energy between the ion and the surrounding water molecules already properly reordered. In the present work the ion-solvent contribution to the solvation energy is calculated by determining the potential energy of the ion in its hydration shell according to

\[
U_{\alpha}^{solv} = 4\pi \sum_{\beta=O,H} \rho_\beta \int_0^\infty dr r^2 g_{\alpha\beta}(r) u_{\alpha\beta}(r).
\]

(6)
The results for the $Na^+$- and the $Cl^-$-ion are presented in table [V]. $U_{\alpha}^{solv}$ is dominated by the Coulomb potential close to the ion. The orientation of water dipoles around the smaller $Na^+$-ion is more pronounced due to the strong electric field and therefore $U_{\alpha}^{solv}$ is more negative for the $Na^+$-ion. Our value $U_{Na^+}^{solv} = -8.60 \text{eV}$ is close to the result of Chandrasekhar et al. [34] for the rigid TIPS-water model.

The total work required to bring an additional ion into the system is given by the chemical potential $\mu_\alpha$. The excess part $\mu_\alpha^{ex}$ due to particle interactions can be determined from the two-particle correlation functions [36] and in case of the HNC-approximation this relation reads

$$\mu_\alpha^{ex} = 2\pi \sum_{\beta=H,O,ion} \rho_\beta \int_0^{\infty} dr \int_0^{\infty} dt \left[ \rho_{\alpha\beta}(r) - g_{\alpha\beta}(r) c_{\alpha\beta}(r) - c_{\alpha\beta}(r) \right].$$  

(7)

In addition to the potential energy gain $U_{\alpha}^{solv}$ of the ion due to ion-water interactions the excess part $\mu_\alpha^{ex}$ of the chemical potential includes also the work required for creating a cavity for the ion in the water network and therefore $\mu_\alpha^{ex}$ must be less negative than $U_{\alpha}^{solv}$. Our value $\mu_{Na^+}^{ex} = -3.23 \text{eV}$ follows this prediction and is in good agreement with the value $-3.93 \text{eV}$ determined experimentally for the free energy of solvation of a $Na^+$-ion [37].

Around the $Cl^-$-ion (cf. Fig. 2a) hydrogen atoms are arranged in two distinctly separated shells and the corresponding oxygen atoms are located in between. This distribution of atoms can be interpreted in terms of a water configuration in the anionic hydration shell where one hydrogen atom of the water molecule is directed into the liquid while the second is pointing towards the $Cl^-$-ion. Similar structural results were observed in analogous computer simulation studies [28,29] and in neutron diffraction experiments [38]. Due to such almost linear orientation of one oxygen-hydrogen bond towards the chloride ion each water molecule in the first $Cl^-$-hydration shell should contribute only with one hydrogen and one oxygen atom to the first $g_{ClH}(r)$- and $g_{ClO}(r)$-maximum. This is expressed by the calculated coordination numbers $N_{ClH} = 18.2$ and $N_{ClO} = 17.9$, although in comparison with the computer simulation result [33] they are too large. This discrepancy may be attributed to the chosen ion-water pair interactions and to the HNC-approximation employed in the integral equation procedure. The coordination numbers are very sensitive on the details of the pair distribution functions, especially on the position and the magnitude of both the first $g_{\alpha\beta}(r)$-maximum and -minimum. As the size of the ion increases the coordination numbers increases too because of an increasing volume available for water molecules in the first hydration shell. On the other hand the resolution of the first hydration shell decreases, as exemplified by the weak coordination plateau in $Cl^-$-hydration shell presented in Fig. 2b, because of the weaker electrostatic attraction. As a result of the overpopulation of the anionic hydration shell, we obtain rather large values of $U_{Cl^+}^{solv} = -7.34 \text{eV}$ and $\mu_{Cl^+}^{ex} = -6.25 \text{eV}$ compared with computer simulation results (cf. table [V]) and the experimental value of $-3.53 \text{eV}$ for the free energy of solvation [37]. With the RISM integral equation method Pettitt et al. [28] calculated for the $Cl^-$-ion a more negative ion-water contribution to the solvation energy than for the $Na^+$-ion. This is clearly in disagreement with several computer simulations and contradicts the idea, that the solvation shell of the smaller cation should be bound more strongly because of the larger electrostatic attraction. The too short chloride-hydrogen distance might be the reason for their very large value of $U_{Cl^+}^{solv}$.

The calculated structural properties of the ionic hydration shells for a dilute aqueous solution of sodium chloride are summarized in table [I] and compared with available experi-
mental data obtained by x-ray or neutron diffraction techniques and with computer simulation and other integral equation results. The results for the position of the first ion-oxygen and ion-hydrogen peaks are in good agreement with the experimental data and with those obtained by Smith et al. using the same CF-water model but different ion-water pair potentials. In the calculation of Thuraisingham et al. all bulk correlation functions, in particular for CF-water, are obtained with the HNC-approximation. This approximation does not reproduce the structural features of bulk water. As a result the number of oxygen atoms in the first hydration shell is overestimated. An improvement is achieved in the present work by adding appropriate bridgefunctions in the closure relation for the water correlation functions. Also some results of an integral equation theory (RISM) for interaction site fluid models are added in table.

Since in a dilute ionic solution only a few water molecules are interacting directly with the ion, the pair distribution functions \( g_{HH}, g_{OH}, \) and \( g_{OO} \) are indistinguishable from those of pure water reported in [1].

The averaged structural effects of the solvent on the ion-ion interactions may be discussed in terms of the potential of mean force (PMF), defined as

\[
W_{\alpha\beta}(r) = -k_B T \ln g_{\alpha\beta}(r).
\]

Our results for the potential of mean force (cf. Fig.3 and Fig.4) show some characteristic structure due to the molecular nature of the solvent. In comparison with the bare pair interaction potential \( u_{\alpha\beta}(r) \), plotted in Fig.3b, the first minimum of \( W_{NaCl}(r) \) is drastically reduced in magnitude and slightly shifted towards larger \( r \)-values. This strongly reduced attraction between the \( Na^+ \)- and \( Cl^- \)-ion at contact arises primarily from a partial overlap of the hydration shells of the single ions. Debye-Hückel screening is of minor importance. The first minimum of \( W_{NaCl}(r) \) at \( r = 3.42 \) Å represents the 'contact ion pair' (CIP), whereas the second minimum at \( r = 5.36 \) Å corresponds to the 'solvent separated ion pair' (SSIP), suggesting a solvation bridge between the sodium and the chloride ion. A combination of the configurations depicted in Fig.1a and Fig.2a for one bridging water molecule explains the position of the SSIP-minimum. For the intervening water molecule a position is energetically more favourable, where the orientation matches those in the hydration shell of a single \( Na^+ \)- and \( Cl^- \)-ion. Therefore the water molecule is slightly displaced from the line connecting both ion centers and the hydrogen atoms are orientated towards the \( Cl^- \)-ion. This interpretation is in line with a previous molecular dynamics simulation, where the solvent configuration due to the minima of \( W_{NaCl}(r) \) is inspected.

The relative depth of the minima determines the stability of the CIP- and the SSIP-state. In our calculation with the CF-water model the first minimum of \( W_{NaCl}(r) \) is found to be deeper than the second. The barrier for ionic dissociation (CIP \( \rightarrow \) SSIP) is 0.97 kcal/mol and for ionic association (SSIP \( \rightarrow \) CIP) 0.30 kcal/mol. The barrier for the dissociation process is higher than for the association process and the CIP state is the most stable configuration. An indication whether the associated or the dissociated state is preferred by the sodium-chloride ion pair is provided by the ionic association constant

\[
K_a = 4\pi N_A \int_0^R d r \ r^2 \exp \left[ - \frac{W_{NaCl}(r)}{k_B T} \right],
\]

where \( N_A \) denotes the Avogadro constant and \( R \) is the position of the barrier maximum seperating the SSIP- from the CIP-state. For the 0.01 molar solution of sodium chloride we
obtain \( K_a = 10.13 \text{l/mol} \). In a dilute ionic solution with concentration \( c \) the coordination number \( K_a \times c \) is interpreted as the fraction \( \theta \) of unlike CIP-pairs in the system. Recent MD simulations suggest the tendency for ion pairing to increase when the dipole moment of the water molecule decreases \[1\]. Compared to the dipole moments of the water models employed in these simulations the mean dipole moment of the flexible CF-water molecule in the fluid phase \((\langle \mu \rangle = 2.154 \text{D})\), which is deduced from our pair distribution functions calculated with the HNC+B-approximation, is smaller. Our larger value for \( K_a \), when compared with the simulation results, is therefore consistent with the higher probability of the CIP configuration when water models with a smaller dipole moment are employed.

Despite the purely repulsive nature of the pair interaction between like ions, the respective potentials of mean force, as plotted in Fig.4, show some oscillatory structure. The existence of minima in the PMFs indicates ion pairing resulting from a subtle balance between the interionic repulsion and an effective attraction mediated by the ionic solvation shells. The PMF for \( Na^+-Na^+ \) and for \( Cl^-\cdot Cl^- \) are significantly different. The tendency for solvent-bridged sodium ion pairing is rather weak as indicated by the shallow minimum of \( W_{NaNa}(r) \) at \( r = 4.52\text{Å} \) and around \( 6\text{Å} \). These positions are in fairly good agreement with a previous computer simulation using the CF-model \[24\]. The first minimum of \( W_{NaNa}(r) \) corresponds to a configuration where a water molecule is in a bridge position between the two sodium ions with the hydrogen atoms pointing into the liquid \[13\]. In contrast to the \( W_{NaNa}(r) \) our calculated \( W_{ClCl}(r) \) possesses a prominent stable minimum at \( r = 6.6\text{Å} \). With the characteristic bond lengths in the chloride-water dimer we found this position consistent with a configuration where a water molecule is placed between the chloride ions orientating each of its hydrogen atoms towards one of the ions. The water molecule serves as a bridge in the chloride ion pair. The relative stability of the solvent-bridged chloride ion pair is known from neutron scattering experiments on highly concentrated electrolyte solutions. The \( Cl^-\cdot Cl^- \) pair distribution function extracted from the measured partial structure factors shows a prominent peak at \( r = 6.1\text{Å} \) for the aqueous solution of \( Ni_2Cl \) \[14\] and at \( r = 6.4\text{Å} \) for the \( LiCl \)-solution \[45\]. In addition to the ‘dilute peak’ around \( 6\text{Å} \), a second maximum of \( y_{ClCl}(r) \) is observed in neutron scattering experiments at \( r = 3.75\text{Å} \) only for high ionic concentration. This peak is reminiscent of the molten salt regime and diminishes as the solution becomes more dilute. The RISM integral equation approach predicts only one stable minimum of the \( Cl^-\cdot Cl^- \) PMF at \( r = 3.5\text{Å} \) even at infinite dilution and obviously fails to reproduce the ‘dilute peak’ \[26\]. Although the positions of stable minima of the PMF are solely determined by the specific ion-water interactions, we found that the depth of the minima and therefore the stability of the ion pairs depend strongly on the ion concentration and the approximations employed in the integral equation calculations.

III. THE ELECTROLYTE AT THE ELECTRODE

A. Computational method. Several integral equations for calculating the density profiles at an electrode-electrolyte interface exist. A first relation between the particle density \( \rho_\alpha(1) \) and the potential energy \( V_\alpha(1) \) of a particle at coordinate 1 due to an external potential, e.g. the electrode, is given by the Born-Green-Yvon (BGY) equation \[16\]
\[ \nabla_1 \ln \rho_\alpha(1) = - \frac{1}{k_B T} \left[ \nabla_1 V_\alpha(1) + \sum_\beta \int d2 \rho_\beta(2) g_{\alpha \beta}(1, 2; [\rho]) \nabla_1 u_{\alpha \beta}(1, 2) \right], \]  

(10)

where \( u_{\alpha \beta}(1, 2) \) is the pair potential and \( g_{\alpha \beta}(1, 2; [\rho]) \) denotes the pair distribution function in the inhomogeneous density distribution in front of the electrode. The functional dependence of \( g_{\alpha \beta} \) on the whole set of one-particle densities \( \{ \rho_\gamma(1) \} \) is indicated by the notation \( g_{\alpha \beta}(\ldots; [\rho]) \). By density functional arguments \[12,13\] an alternative to the BG Y-equation can be derived, where the density profile is related to the direct correlation function \( c_{\alpha \beta} \) instead of the total correlation function \( h_{\alpha \beta} \).

\[ \ln \left[ \frac{\rho_\alpha(1)}{\rho_\alpha} \right] = - \frac{1}{k_B T} V_\alpha(1) + \sum_\beta \int d2 [\rho_\beta(2) - \rho_\beta] \int_0^1 d\lambda c_{\alpha \beta}(1, 2; [\rho_\lambda]). \]  

(11)

This equation is exact too, but requires a functional integration of the direct correlation function over a sequence of density distributions \( \{ \rho_\lambda \} = \{ \rho_\gamma(1; \lambda) \} \) from the initial state (\( \lambda = 0 \), e.g. the homogeneous fluid, to the final state (\( \lambda = 1 \), when the external potential is completely switched on. By the same density functional arguments an even simpler relation between the density gradient and the external potential can be obtained, which avoids the functional integration. Originally this equation was derived by Wertheim [47] and independently by Lovett, Mou and Buff [48] for simple fluids, hereafter called the WLMB-equation. In the generalisation for a particle mixture the WLMB-equation reads

\[ \nabla_1 \ln \rho_\alpha(1) = - \frac{1}{k_B T} \nabla_1 V_\alpha(1) + \sum_\beta \int d2 c_{\alpha \beta}(1, 2; [\rho]) \nabla_2 \rho_\beta(2). \]  

(12)

In contrast to eq.(11) the BGY- and WLMB-equation require only the inhomogeneous particle-particle correlations in the final density distribution near the electrode and not for a sequence \( \{ \rho_\lambda \} \) of densities. Calculating the inhomogeneous particle-particle correlation functions from the Ornstein-Zernike equation requires great computational effort. Only for much simpler systems like the primitive model electrolyte in contact with a hard wall, this complicated calculation has been done [19]. For this reason several approximations for the inhomogeneous particle-particle correlations have been applied in the density profile equations (10)-(12). Our experience has lead us to the conclusion that an approximation of the direct correlation function \( c_{\alpha \beta}(1, 2; [\rho]) \) is more robust than of the total correlation function \( h_{\alpha \beta}(1, 2; [\rho]) \) [50,51]. In the simplest approximation the inhomogeneous direct correlation function is replaced by its uniform-fluid counterpart

\[ c_{\alpha \beta}(1, 2; [\rho]) \approx c_{\alpha \beta}(1, 2; \{ \rho_\gamma \}) = c_{\alpha \beta}(1, 2). \]  

(13)

Going a step further, the inhomogeneous direct correlation functions can be locally approximated by correlation functions of the homogeneous fluid evaluated at appropriate weighted densities [12,50,52]. For our complex model electrolyte we have achieved very good results using the approximation (13). Especially the ice-like water layers in the vicinity of the electrode were formed [1]. On this stage of approximation eq.(11) and the WLMB-equation (12) become equivalent. For numerical application we prefer the WLMB-equation.

Considering a planar electrode perpendicular to the z-axis of a Cartesian coordinate system, the one-particle density \( \rho_\alpha(1) \) and the external potential energy \( V_\alpha(1) \) are functions
of $z$ only. The gradient is a derivative with respect to $z$ and the integration perpendicular to the $z$-axis can be carried out separately. This leads to the WLMB-equation in the form

$$\frac{d \ln \rho_\alpha(z_1)}{dz_1} = -\frac{1}{k_B T} \frac{d V_\alpha(z_1)}{dz_1} + 2\pi \sum_\beta \int_{-\infty}^{\infty} dz_2 \frac{d \rho_\beta(z_2)}{dz_2} \int_{|z_1-z_2|}^{\infty} dr \, c_{\alpha \beta}(r). \quad (14)$$

Since our model electrolyte consists of charged particles, eq. (14) contains diverging terms due to the Coulombic interactions. For an analytical treatment of these long-range terms separating the short-range part and the Coulombic tail of the direct correlation function, as proposed by Ng [53], is appropriate

$$c_{\alpha \beta}(r) = c_{\alpha \beta}^{SR}(r) - \frac{q_\alpha q_\beta \, \text{erf}(\lambda r)}{k_B T r}, \quad (15)$$

where $\text{erf}(\lambda r)$ is the error-function. With the definition of the charge density $q(z) = \sum_\alpha q_\alpha \rho_\alpha(z)$ the diverging Coulombic terms are collected under the sum over $\beta$. Requiring bulk neutrality ($\rho_\alpha(z) \to 0$ as $|z| \to \infty$) and $\rho_\alpha(z \leq 0) = 0$ in the left halfspace, the charge density vanishes on the boundaries of the integral and integration by parts yields

$$\frac{d \ln \rho_\alpha(z_1)}{dz_1} = -\frac{1}{k_B T} \frac{d V_\alpha(z_1)}{dz_1} + 2\pi \sum_\beta \int_{-\infty}^{\infty} dz_2 \frac{d \rho_\beta(z_2)}{dz_2} \int_{|z_1-z_2|}^{\infty} dr \, c_{\alpha \beta}^{SR}(r)$$

$$+ \frac{2\pi q_\alpha}{k_B T} \int_{-\infty}^{\infty} dz_2 q(z_2) \, \text{sgn}(z_1 - z_2) \, \text{erf}(\lambda |z_1 - z_2|). \quad (16)$$

In order to investigate the influence of an external electric field on the structural properties of the electrode-electrolyte interface, the electrode is covered with a homogeneous charge density $\omega$:

$$V_\alpha(z_1) = V_\alpha^{SR}(z_1) - 2\pi q_\alpha \omega z_1. \quad (17)$$

The repulsive nature of the electrode or some specific chemical bonding is incorporated in the short ranged interaction potential $V_\alpha^{SR}(z_1)$. Under the constraint of exact compensation of the surface charge density by charges in the fluid, the mean electric field due to the charge distribution in the right halfspace ($z_1 \geq 0$)

$$E(z_1) = -4\pi \int_{z_1}^{\infty} dz_2 q(z_2). \quad (18)$$

satisfies the boundary condition $E(z_1 = 0) = 4\pi \omega$ at the electrode. With this assumption, using eq.(17) and eq.(18) and introducing the complementary error-function $\text{erfc}(x) = 1 - \text{erf}(x)$, equation (14) can be rewritten in the form

$$\frac{d \ln \rho_\alpha(z_1)}{dz_1} = -\frac{1}{k_B T} \frac{d V_\alpha(z_1)}{dz_1} + \frac{q_\alpha E(z_1)}{k_B T} + 2\pi \sum_\beta \int_{-\infty}^{\infty} dz_2 \frac{d \rho_\beta(z_2)}{dz_2} \int_{|z_1-z_2|}^{\infty} dr \, c_{\alpha \beta}^{SR}(r)$$

$$- \frac{2\pi q_\alpha}{k_B T} \int_{-\infty}^{\infty} dz_2 q(z_2) \, \text{sgn}(z_1 - z_2) \, \text{erfc}(\lambda |z_1 - z_2|). \quad (19)$$

The information about particle-particle correlations are contained in the short ranged part of the direct correlation functions, calculated seperately from the Ornstein-Zernike equation.
for the homogeneous mixture as discussed in section II. Starting with bulk density \( \rho_\alpha \) at \( z_1 \to \infty \) an integration yields the density profile

\[
\rho_\alpha(z_1) = \rho_\alpha - \int_{z_1}^{\infty} dz_2 \frac{d\rho_\alpha(z_2)}{dz_2}.
\] (20)

The set of coupled WLMB-equations (19) was solved iteratively applying a standard mixing scheme to stabilize the iteration procedure. In each iteration step the condition of charge neutrality has been carefully controlled. With this method the density profiles for an aqueous solution of sodium chloride in contact with an uncharged and charged electrode are calculated. The electrode was assumed unpolarizable. The short-range interaction \( V_\alpha^{SR}(z) = A/z^9 \) \( (A = 1.88 \times 10^{-14} \text{erg}) \) of the electrode is purely repulsive and equal for all particles. This fast decaying repulsive potential is very similar to a hard wall, but convergence of the iteration scheme is achieved more rapidly for the 'soft' wall.

**B. Results for the uncharged electrode.** Fig.5a shows the density profiles for sodium and chloride ions as well as for the hydrogen and oxygen atoms calculated for the 0.01 molar solution at the uncharged, repulsive electrode. In front of the electrode there is a densely packed water layer. About 3Å apart a second less densely packed layer is found. This distribution of hydrogen and oxygen atoms resembles the density profiles obtained for pure water at the same type of wall, which have been interpreted in terms of an ice-like water structure [1]. In comparison to these previous calculations the density of the first water layer is slightly reduced. Both ion species are strongly repelled by this densely packed water layer. In the region of the second water layer sodium ions are found with almost the same probability as in the bulk, whereas the larger chloride ions are still hindered from penetrating into this part of the interfacial region. Since the electrode acts equally repulsive on both ion species, steric and electrostatic interactions between the differently sized ions and the ice-like water matrix are responsible for the difference in the ionic density profiles.

Information about the water structure is obtained by inspecting the charge density \( q(z) = q[\rho_H(z) - 2\rho_O(z)] \). In Fig.5b this difference of particle densities is plotted for the water solvent in the electrolyte and for pure water. Both charge density profiles are very similar; that means the water structure at the electrode is not much perturbed by the presence of ions. The sequence of positive and negative charge density is characteristic for the ice structure. An schematic illustration of the ice structure can be found for example in reference [1]. Each water molecule provides two hydrogen atoms and two 'lone pair'-valencies in tetrahedral geometry. Since reorientation of water molecules without disrupting the hydrogen bonded network is possible under the constraint that each hydrogen bond is occupied by only one hydrogen atom, the ice structure has some internal polarizability. Thus the ice-like water structure can persist also under the influence of external electric fields. The charge density profile of water at a planar electrode has been already discussed in detail previously [1]. Here, we briefly review the most important structural features: i) the broad density peak at contact actually consists of two oxygen layers with hydrogen atoms in between. In this double layer water molecules are connected by hydrogen bonds strongly tilted with respect to the surface normal. This yields a very small distance between the oxygen layers. ii) The detailed structure of another water double layer around 4Å, where the negative charges dominates, is not clearly resolved in the charge density profiles. iii) The low density region
between the double layers is characterized by the pronounced double maximum of positive charge density. Hydrogen atoms are arranged in two layers, forming hydrogen bonds between successive water double layers. iv) The calculated water structure at the electrode starts with a layer of oxygen atoms. Since our model electrode acts purely repulsive on all particles, it is energetically more favourable for water molecules immediately at the electrode to place their hydrogen atoms into hydrogen bonds within the first water double layer. Therefore the orientation of the first water layer is fixed by the water structure and this yields a spontaneous net polarization or surface potential of the electrode-water interface, even at the uncharged electrode. Due to the strong inclination of hydrogen bonds within the water double layer, the dipole moment of water molecules at contact is only slightly orientated towards the bulk fluid.

The structural and electrostatic properties of the ice-like water significantly affects the distribution of the solute in the electrode-electrolyte interface (cf. Fig.5a). It is of particular importance for the interfacial ionic distribution how the differently sized ions fit into the ice-like water structure. For instance, the smaller Na\(^+\)-ion (\(\sigma_{Na^+} = 2.4\,\text{Å}\)) penetrates into the second water double layer around 4 Å. The hexagonal water coordination within a double layer is wide and flexible enough, so that the ion is able to slip into the region between the first and second water double layer. In this region the water structure has still enough flexibility to match the geometry of the Na\(^+\)-solvation shell without disrupting the hydrogen bonded network. The seperation between the first and second water double layer increases slightly. Simultaneously positively charged hydrogens are transferred from this interlayer region into both neighbouring water double layers (cf Fig.5b). But the ice-like sequence of positive and negative charge density still persists. The redistribution of positive charges can be interpreted as a reorientation of water molecules to optimize their interaction with the neighbouring sodium ion. Water molecules of the upper and lower double layer locally provide an environment for the Na\(^+\)-ion, which resembles the bulk solvation shell and is also compatible with the ice structure. Therefore the local density \(\rho_{Na}(z)\) is close to its bulk value. In the region between the first and the second water double layer the mean electrostatic potential (cf. Fig.5) becomes repulsive for the Na\(^+\)-ion due to the large number of positively charged hydrogen atoms arranged in hydrogen bonds connecting successive water double layers. Although the Na\(^+\)-ion, when further approaching the electrode, is attracted by the net dipol moment of the first water double layer, penetration into the densely packed first water double layer can be only accomplished by a strong, local distortion of the ice-like ordering. But in this region the ice structure is rather rigid and the approach of the ion is therefore strongly hindered.

The behaviour of the larger Cl\(^-\)-ion (\(\sigma_{Cl^-} = 3.24\,\text{Å}\)) in the electrode-electrolyte interface is quite different. The chloride ion is too large for the hexagonal rings of hydrogen bonded water molecules, already in the partially disordered second water double layer. In order to provide a proper solvation environment for the Cl\(^-\)-ion hydrogen bonds have to be disrupted, which is energetically unfavourable and therefore the density \(\rho_{Cl}(z)\) decreases in the interfacial region. Although the mean electrostatic potential (cf. Fig.5) becomes attractive for the Cl\(^-\)-ions in the interlayer region, the rigidity of the ice-like water structure and thus the steric repulsion increases. These competitive interactions yields the local maximum of \(\rho_{Cl}(z)\) around 4 Å. Additional chemical ion-surface or image interactions with a metal electrode can overcome the repulsion of the rigid water layer [24]. At a more realistic electrode
contact adsorption is expected for the larger Cl\textsuperscript---ion [22].

The mean electrostatic potential across the interface

\[ \Psi(z_1) = \int_{z_1}^{\infty} dz_2 E(z_2) = 4\pi \int_{z_1}^{\infty} dz_2 (z_1 - z_2) q(z_2) \]  

(21)
is plotted in Fig. 6 for the electrolyte and for pure water. The shape and the magnitude of both curves are very similar throughout the entire interface. Adding ions to the water reduces the potential drop across the first water double layer, indicating a decreased surface dipole moment due to the reorientation of water molecules in order to optimize their interactions with sodium ions in the neighbourhood. The contribution of the ionic charges to \( \Psi(z) \) is rather small because of the very low ion densities, especially near the electrode. The total dipole moment due to the charge density in the interfacial region is given by the overall electrostatic potential drop across the interface

\[ \int_{\infty}^{0} dz z q(z) = \Psi(0) = \frac{\Psi_0}{4\pi}, \]  

(22)
i.e. the work required to move a test charge from the bulk liquid with \( \Psi(z = +\infty) = 0 \) to the electrode. In the literature the potential drop \( \Psi_0 \) at zero surface charge density is sometimes denoted as the 'potential of zero charge'. In electrochemistry the measured 'potential of zero charge' (PZC) means a different quantity (cf. Fig. 7). Often the 'surface potential' \( \chi \) is used, which is related to \( \Psi_0 \) for the uncharged electrode by the sign convention \( \chi = -\Psi_0 \). Our value \( \Psi_0 = -74 \text{mV} \) for the electrode-electrolyte interface is somewhat smaller in magnitude than \( \Psi_0 = -110 \text{mV} \) calculated previously for pure water [1]. The negative sign of \( \Psi_0 \) reflects the preference of the water oxygens close to the surface. Our surface potential for water at a planar, inert wall agrees in sign with the surface potential for the liquid-vapor interface predicted from theoretical and experimental data [54], and with the surface potential obtained by Torrie and coworkers for a water-like solvent model with multipolar hard spheres [18]. Recently Booth et al. have calculated \( \Psi_0 \) according to eq. (22) using eq. (11) with bulk correlation functions for determining the density profiles of hydrogen and oxygen atoms for the central force water in contact with a quasi-hard wall [55]. Their value \( \Psi_0 = +600 \text{mV} \) has the opposite sign. From the corresponding curve for the electrostatic potential, presented in Fig.6a of reference [55], together with the Poisson equation, which relates the curvature of the mean electrostatic potential to the charge density \( q(z) \), it follows a reversion of the surface dipole moment in disagreement with our and other results [18]. The reason for this reverted orientation is not quite clear, because Booth and coworkers used a model and computational treatment completely equivalent to our procedure. Only the particle-particle correlations taken from the bulk might be different. According to our understanding, the driving force for the spontaneous polarization of the electrode-water interface is the tendency of the interfacial water structure to maximize the number of hydrogen bonds [1].

C. Results for the charged electrode. In this section we discuss the influence of an external electric field due to an electrode covered with a constant charge density on the distribution of ions in the electrode-electrolyte interface. The surface charge density \( \omega \) is increased up to \( \omega = \pm 10.4 \mu\text{C/cm}^2 \) corresponding to an electric field strength of \( 1.18 \times 10^8 \text{V/cm}, \)
comparable to a very strong electric field applicable in electrochemical experiments. Our previous calculations for pure water have shown that the ice-like water structure near the electrode is preserved under the influence of such field strengths. The reorientation and the exchange of hydrogen atoms between the two positions in a hydrogen bond provides for enough polarizability. In case of a small negative surface charge density alignment of water dipoles with respect to the electric field is hindered. For the hydrogen atoms of the contact water layer it is energetically more favourable to remain still between the oxygen layers as long as the energy gain in the external potential is smaller than the binding energy in the hydrogen bond. Therefore the polarizability decreases. Only when the hydrogen bond energy is overcompensated by the potential energy gain of the hydrogen atom in the external field, some hydrogens follow the attractive electric field. As a result the interfacial polarizability increases. This reorientation of water molecules starts at \( \omega = -3.7 \mu C/cm^2 \). Experimental and theoretical investigations found a maximum of the interfacial entropy for surface charge densities in the range from \(-4 \) to \(-6 \mu C/cm^2 \), where the hydrogen atoms of the contact water layer, according to our calculations, can occupy two different positions. The mechanism of water reorientation still holds for the water solvent in the electrode-electrolyte interface. The ion density profiles, presented in Figure 8, have to be discussed with respect to this specific behaviour of water molecules in an applied electric field. For a surface charge density \( \omega > 0 \) the electric field cannot force the large \( \text{Cl}^- \)-ion to penetrate into the contact water layer, whereas an electric field of opposite sign but of same magnitude brings the \( \text{Na}^+ \)-ion close to the electrode surface. This different ability of approaching the electrode is a result of two competing forces: the attraction due to the external electric field and the steric repulsion of the differently sized ions by the ice-like water matrix established in front of the electrode. When the external field is attractive enough for the hydrogen atoms of contact water molecules to flip towards the electrode, the \( \text{Na}^+ \)-ions finally invade the first water double layer and even get into contact with the surface (cf. dashed-dotted line in Fig.8a). A measure for the excess of ions in the electrode-electrolyte interface is

\[
\Gamma_\alpha = \int_0^\infty dz \left[ \rho_\alpha(z) - \rho_\alpha \right]. \quad (23)
\]

The plot of \( \Gamma_\alpha \) for the \( \text{Na}^+ \)-ions vs \(-\omega \) in the inset of Fig.8a reflects the rapidly increasing penetration of \( \text{Na}^+ \)-ions into the surface water structure beyond \( \omega \approx -4 \mu C/cm^2 \), where the pronounced water reorientation becomes significant. Contact adsorption of \( \text{Na}^+ \)-ions has been also observed in computer simulations [23].

In order to elucidate the effect of the asymmetric response of ionic charges in an applied electric field on the differential capacitance \( C = \partial \omega / \partial \Psi_0(\omega) \), we evaluated \( \Psi_0(\omega) \) across the interface for a series of surface charge densities. Some of these values \( \Psi_0 \) are summarized in table V. For comparison the last column of table V shows the values of \( \Psi_0(\omega) \) for pure water. As already mentioned, at zero surface charge the electrostatic potential drop across the interface is only slightly smaller than for pure water, but the negative sign is retained. The same trend was observed by Torrie and coworkers when adding ions to their multipolar, water-like solvent model [18]. In the third column we have listed the change \( \Delta \Psi_0 = \Psi_0(\omega) - \Psi_0(\omega = 0) \). Only for small surface charge densities \( |\Delta \Psi_0| \) behaves like a symmetric function of \( \omega \), whereas for large negative surfaces charges \( |\Delta \Psi_0| \) grows more strongly than for corresponding \( \omega > 0 \). This implies a smaller differential capacitance for
the negatively charged electrode. In order to decide whether this asymmetry is due to the response of the water solvent or due to the ions, we have examined the water and ionic contributions to the mean electrostatic potential $\Psi_0(\omega)$ separately, as shown in table [V]. For the 0.01 molar solution the ionic contribution $\Psi_{\text{ionic}}$ is rather small in comparison with $\Psi_{\text{water}}$. For almost all surface charge densities $\Psi_{\text{ionic}}$ is independent of $\omega$. Only the pronounced adsorption of $Na^+$-ions yields a distinct increase in $\Psi_{\text{ionic}}$. Since $\Psi_{\text{ionic}}$ is rather small and flat, the asymmetric response of the total $\Psi_0(\omega)$ is primarily a property of the interfacial water structure. Nevertheless, to some extent $\Psi_{\text{water}}$ is indirectly affected by the presence of ions through a restructuring of the contact double water layer, as emphasized by comparing the solvent component $\Psi_{\text{water}}$ and $\Psi_0(0 M)$ for pure water. $\Psi_{\text{water}}$ for the electrolyte varies less strongly with respect to $\omega$. As a result the differential capacitance for the electrode-electrolyte interface is larger than for pure water over the whole range of considered surface charge densities.

The differential capacitance $C = \partial \omega / \partial \Psi_0(\omega)$ obtained from the derivative of a cubic spline fit to the $\Psi_0(\omega)$ data is shown in Fig.9 as a function of surface charge density $\omega$. The curves for the 0.01 molar aqueous solution of sodium chloride and for pure water, taken from [1], are very similar. Because $\partial \Psi_{\text{ionic}}(\omega)/\partial \omega$ is negligible in comparison with $\partial \Psi_{\text{water}}(\omega)/\partial \omega$, the total capacitance of the electrode-electrolyte interface is dominated by the response of the interfacial water structure. The minimum in the differential capacitance curve has been identified with the beginning of water reorientation in the adsorbed water layer [1]. The asymmetry in the differential capacitance curve with respect to zero surface charge and the existence of a minimum at negative surface charge density are typical of the experimental data for simple electrolytes [11]. It has been argued that the asymmetry is a consequence of ionic polarizability or of ion-specific interaction with the electrode [56]. Our result suggest that the minimum can be explained by the asymmetric water response near an electrode, at least for low concentrated electrolytes. We found the differential capacitance for the electrolyte larger than for pure water over the whole range of surface charges considered, indicating an overall larger polarizability of the interfacial structure. From the rather small direct effect of the ion distribution on the differential capacitance, we infer that due to the presence of sodium and chloride ions in the interface water molecules are already reorientated and less strongly fixed within the ice-like water structure yielding a larger polarizability of the interfacial water structure.

IV. CONCLUSIONS

We have extended our previously developed integral equation method for calculating bulk correlation functions and density profiles for the central force water model to a detailed microscopic model of an aqueous electrolyte. Spherical symmetric pair potentials for the additional ion-ion and ion-water interactions are designed to represent the different size of sodium and chloride ions as well as the orientation of water molecules around both ions. Only for the water correlation functions we have added to the HNC-approximation appropriate bridgefunctions, which are optimized in order to yield the bulk water structure [1]. The calculated ion-water pair distribution functions reflects specific features of the ionic hydration shells in aqueous solutions. On average six water molecules are located in the
first $Na^+$-hydration shell and their dipole moment is tilted with respect to the ion-oxygen radial vector. The water molecules around the larger $Cl^-$-ion are bound more weakly and therefore the first hydration shell of the anion is less sharply defined. We have found that in the anionic hydration shell the water molecules are orientated with one of the hydrogen atoms towards the $Cl^-$-ion.

Taking these correlation functions of the homogeneous fluid for describing the particle-particle correlations near the electrode, we have calculated the density profiles for the various particle species near a planar electrode, which is neutral or charged and has some hard wall repulsion, equal for all particles. The charge density profile of the water solvent that is established at a neutral electrode resembles that for pure water, which has been interpreted in terms of an ice-like arrangement of water molecules [1]. This layered structure extends about two water double layers into the liquid. Water molecules adjacent to the surface are slightly orientated toward the bulk fluid and thus the interfacial water structure is polarized, even without any external electric field. This specific water structure induces an asymmetric ion distribution in front of the electrode depending strongly on the ion size. The smaller $Na^+$-ion can easily penetrate into the second water double layer and even comes into contact with the surface for sufficiently attractive fields. Penetration of the larger $Cl^-$-ion into this interfacial region is strongly hindered. Strong local, steric interactions between the ions and the ice-like water structure dictates this different behaviour. Electrostatic effects are only of minor importance. The cavities formed by the puckered hexagonal water rings within a water double layer are wide and flexible enough to match the size of the smaller $Na^+$-ion. Water molecules are reorientated without disrupting the ice structure in order to provide a solvation environment for the $Na^+$-ion. This reorientation of water molecules is responsible for a reduction of the surface potential from $\Psi_0 = -110 \text{ mV}$ in case of pure water to $\Psi_0 = -74 \text{ mV}$ calculated for the 0.01 molar solution of sodium chloride at the uncharged electrode. The $Cl^-$-ion is too large for the rigid hexagonal water cavities and therefore the $Cl^-$-ions are strongly repelled.

Under the influence of an external electric field of reasonable strength the ice-like water structure near the electrode is still preserved. Chloride ions are less effectively attracted by a positively charged electrode than sodium ions by an equivalently attractive electric field because the rigid first water double layer resists the electric field. On the other hand $Na^+$-ions suddenly penetrate into the contact water layer, when the electrode charge is large enough ($-4 \mu C/cm^2$) to induce ‘flipping’ of adsorbed water molecules within the ice structure.

Although sodium and chloride ions behaves differently at oppositely charged electrodes, this has a negligible effect on the interfacial differential capacitance $C = \partial \omega / \partial \Psi_0(\omega)$. At least for dilute aqueous electrolytes the asymmetry in the differential capacitance curve with respect to zero surface charge density is solely determined by the ice-like water structure as discussed more extensively in reference [1]. Due to the presence of $Na^+$-ions some water molecules are less strongly fixed within the interfacial water structure and already reorientated in order to optimize their interaction with the neighbouring ion. As a result, we have obtained a larger polarizability and therefore a larger differential capacitance for the electrode-electrolyte interface compared with pure water. Our present model has to be further developed for instance by introducing specific electrode-ion interactions in order to understand more features of the experimental differential capacitance curves microscopically.
ACKNOWLEDGMENTS

Helpful discussions with M. Kasch and J.E. Diaz-Herrera and financial support of this work by Deutsche Forschungsgemeinschaft are gratefully acknowledged.
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FIGURES

FIG. 1. a) Pair distribution functions $g_{NaH}(r)$ (---) and $g_{NaO}(r)$ (− −) for a 0.01 molar aqueous NaCl-solution. b) The corresponding coordination numbers $N_{NaH}(r)$ (---) and $N_{NaO}(r)$ (− −).

FIG. 2. a) Pair distribution functions $g_{CIH}(r)$ (---) and $g_{CIO}(r)$ (− −) for a 0.01 molar aqueous NaCl-solution. b) The corresponding coordination numbers $N_{CIH}(r)$ (---) and $N_{CIO}(r)$ (− −).

FIG. 3. a) The potential of mean force for the ion pair $Na^{+}−Cl^{−}$ and b) the bare interaction potential $u_{NaCl}(r)$.

FIG. 4. The potential of mean force for the ion pairs $Na^{+}−Na^{+}$ (---) and $Cl^{−}−Cl^{−}$ (− −).

FIG. 5. a) The density profile $\rho_{a}(z)/\rho_{a}$ for hydrogen (---) and oxygen atoms (− −), for $Na^{+}$- (· · ·) and $Cl^{−}$-ions (− · −) at the uncharged electrode. b) The charge density $q(z) = q[\rho_{H}(z)−2\rho_{O}(z)]$ for the water solvent in the electrolyte (---) and for pure water (− −).

FIG. 6. The mean electrostatic potential $Ψ(z)$ near an uncharged electrode for pure water (− · −), the 0.01 molar aqueous solution of sodium chloride (---), ionic (− −) and solvent contributions (· · ·).

FIG. 7. Schematic diagram of contributions to the electrochemical potential of an electron. Different contributions are plotted as $−e\phi(z)$. Electrostatic potential (---), potential in front of liquid surface (− −), $Ψ_{0}$: the surface potential of the electrolyte eq.22, PZC: potential of zero charge measured in electrochemistry, $Φ_{i}$: workfunction of the electrodes, $χ_{M}$: surface potential of metal, S: total surface potential at reference electrode, AP: absolute electrode potential at reference electrode related to redox reaction.

FIG. 8. The density profiles for the $Na^{+}$- and $Cl^{−}$-ions at the a) negatively and b) positively charged electrode for surface charge densities $\omega = 0$ (---), $±1.6$ (− −), $±3.2$ (· · ·) and $±6.4 \mu C/cm^{2}$ (− · −). The inset shows $Γ_{Na}(ω)$ as a function of $−ω$.

FIG. 9. The differential capacitance for the 0.01 molar aqueous NaCl-solution and for pure water.
TABLE II. Structural properties of the ionic hydration shell at T=300 K.

|                     | $Na^+$ | $Cl^-$ |
|---------------------|--------|--------|
| ion-oxygen distance in Å |        |        |
| This work           | 2.34   | 3.52   |
| Smith et al.        | 2.33   | 3.40   |
| Pettitt et al.      | 2.30   | 3.45   |
| X-ray               | 2.38 - 2.40 | -  |
| neutron diffraction | -      | 3.2 - 3.34 |
| ion-hydrogen distance in Å |        |        |
| This work           | 2.69 and 3.21 | 2.78 |
| Smith et al.        | 3.0    | 2.53   |
| Pettitt et al.      | 3.05   | 2.0    |
| neutron diffraction | -      | 2.2 - 2.26 |
| coordination number ion-oxygen |        |        |
| This work           | 6.5    | 17.9   |
| Bopp et al.         | 5.9    | 8.4    |
| Thuraisingham et al.| 15.9   | 17.3   |
| Ichiye et al.       | 5.7    | -      |
| Pettitt et al.      | 4.28   | 11.73  |
| X-ray               | 4.6    | -      |
| coordination number ion-hydrogen |        |        |
| This work           | 14.9   | 18.2   |
| Ichiye et al.       | -      | 14.8   |
| Pettitt et al.      | 6.97   | -      |
| neutron diffraction | -      | 5.3 - 6.2 |

$^a$MD, infinite dilution

$^b$RISM, infinite dilution

$^c$MD, 2.2 m NaCl

$^d$HNC, 0.069M NaCl

$^e$RHNC, infinite dilution
TABLE I. Ion-water Lennard-Jones parameters. $\sigma$ in Å and $\epsilon$ in $10^{-12}$ erg.

| $\alpha$ | $\sigma_{\alpha O}$ | $\sigma_{\alpha H}$ | $\epsilon_{\alpha O} = \epsilon_{\alpha H}$ |
|----------|---------------------|---------------------|----------------------------------|
| $Na^+$   | 2.222               | 1.547               | 0.1853                           |
| $Cl^-$   | 3.378               | 2.703               | 0.03708                          |

TABLE III. Orientation of water molecules, mean values of $\Theta$ in degree.

|                | $Na^+$ | $Cl^-$ |
|----------------|--------|--------|
| This work      | 117    | 44     |
| Smith et al.   | 124    | 34     |
| Heinzinger et al. | 139    | 55     |
| Heinzinger et al. | 132    | 54     |

$a$ MD with CF-water, from $g_{\alpha\beta}(r)$

$b$ MD with CF-water, from $\Theta = \cos^{-1}\langle\cos \Theta\rangle$

$c$ same as b with the ST2-water

TABLE IV. Energy of solvation in eV.

|                | $U_{solv}^{Na^+}$ | $U_{solv}^{Cl^-}$ |
|----------------|-------------------|-------------------|
| This work      | -8.60             | -7.34             |
| Chandrasekhar et al. | -8.47 ± 0.04     | -6.21 ± 0.04     |
| Zhu et al.     | -6.92 ± 0.53      | -4.51 ± 0.53      |
| Pettitt et al. | -7.21             | -8.25             |

$a$ MD, 0.444 molal

$b$ MD, 1.791 molal

$c$ RISM, infinite dilution
TABLE V. Surface potential $\Psi_0$, $\Delta \Psi_0 = \Psi_0(\omega) - \Psi_0(\omega = 0)$, ionic and solvent contributions in volts for the 0.01 M aqueous NaCl-solution and $\Psi_0(0 M)$ for pure water.

| $\omega$ [\(\mu C/cm^2]\) | $\Psi_0$ | $\Delta \Psi_0$ | $\Psi_{\text{water}}$ | $\Psi_{\text{ionic}}$ | $\Psi_0(0 M)$ |
|-----------------------------|------------|-----------------|-----------------|-----------------|----------------|
| -10.4                       | -1.039     | -0.9652         | -1.018          | -0.0210         | -1.0890        |
| -6.4                        | -0.670     | -0.5960         | -0.657          | -0.0130         | -0.7140        |
| -3.2                        | -0.371     | -0.2973         | -0.359          | -0.0117         | -0.4119        |
| -2.4                        | -0.296     | -0.2227         | -0.285          | -0.0116         | -0.3364        |
| -1.6                        | -0.222     | -0.1483         | -0.210          | -0.0115         | -0.2608        |
| 0.0                         | -0.074     | 0.0000          | -0.062          | -0.0114         | -0.1100        |
| 1.6                         | 0.073      | 0.1470          | 0.085           | -0.0114         | 0.0402         |
| 2.4                         | 0.146      | 0.2199          | 0.158           | -0.0114         | 0.1149         |
| 3.2                         | 0.219      | 0.2924          | 0.230           | -0.0114         | 0.1895         |
| 6.4                         | 0.504      | 0.5775          | 0.516           | -0.0114         | 0.4847         |
| 10.4                        | 0.849      | 0.9226          | 0.860           | -0.0112         | 0.8464         |
$N_{NaH} = 14.9$

$N_{NaO} = 6.5$
