Coulombic and non-Coulombic effects of single and overlapping Electric Double Layers with Surface Charge Regulation

Raviteja Vangara
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Coulombic and non-Coulombic effects of single and overlapping Electric Double Layers with Surface Charge Regulation

by

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M.S. Chemical Engineering, University of New Mexico, 2017
B.Tech, Chemical Engineering, National Institute of Technology, 2015

DISSEPTION

Submitted in Partial Fulfillment of the Requirements for the Degree of

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December, 2019
Dedication

To my parents, Sujana Kumari and Srinivasulu Vangara, for their support and encouragement

In the loving memory of Varalakshmi Yallapragada (Peddamma) and Sathya Narayana Vadlamudi (Peddamavayya)
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Oh me! Oh life! of the questions of these recurring,
Of the endless trains of the faithless, of cities fill’d with the foolish,
Of myself forever reproaching myself, (for who more foolish than I, and who more faithless?)
Of eyes that vainly crave the light, of the objects mean, of the struggle ever renew’d,
Of the poor results of all, of the plodding and sordid crowds I see around me,
Of the empty and useless years of the rest, with the rest me intertwined,
The question, O me! so sad, recurring—What good amid these, O me, O life?

Answer.
That you are here—that life exists and identity,
That the powerful play goes on, and you may contribute a verse.

- Walt Whitman
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Abstract

The physical origin of charged interfaces involving electrolyte solutions is in the thermodynamic equilibrium between the surface reactive groups and certain dissolved ionic species in the bulk. This equilibrium is very strongly dependent on the precise local density of these species, also known as potential determining ions in the solution. The latter, however, is determined by the overall solution structure, which is dominated by the large number of solvent molecules relative to all solutes. Hence, the solvent contribution to the molecular structure is a crucial factor that determines the properties of electric double layers. Models that explicitly account for the solvent structure are often referred to as ”civilized” as opposed to the ”primitive” ones that consider the solvent as a structureless continuum. A physically correct description of charged interfaces that involve electrolyte solutions (electric double layers), needs to account for the full solution structure in conjunction with the precise surface chemistry governed by the thermodynamic equilibrium.
Apart from charge regulation, these systems involve a wide variety of interactions between the different components of the electrolyte solutions and with the charged interface. While the role of all Coulombic type of interactions is clear, that of the non-Coulombic forces is less obvious. Such as the effects of bulk solvation interactions and solvophobic or solvophillic interactions on the properties of the electric double layer.

This doctoral dissertation presents a comprehensive study of the effects of the non-electrostatic interactions on the electric double layer such as ionic solvation, solvent-solvent interactions and interactions of solution components with the charged surface in Electric double layer. The analysis of electrostatic properties like surface charge and potential, and the distribution of ionic species and total electrostatic charge distribution were presented. The analysis uses classical Density Functional Theory which treats the solvent explicitly and ionic species with finite sizes coupled with surface charge regulation.
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Glossary

\( \Psi \)  Electrostatic Potential

\( \rho^0 \)  Bulk number density of charged species.

\( q_i e \)  Charge of ionic species \( i \).

\( k_B \)  Boltzmann Constant

\( T \)  Temperature

\( \varepsilon \)  Medium dielectric permittivity

\( \varepsilon_0 \)  Dielectric constant of vacuum.

\( \sigma_s \)  Surface Charge

\( \Omega \)  Grand thermodynamic potential

\( F^{id} \)  Ideal contribution of free energy

\( F^{ex}_{HS}, F^{ex}_{long} \)  Excess free energy contribution of Hard-spheres and long range.

\( \rho_e \)  The charge density distribution in solution which is the sum of the density distribution of the species with their respective charge numbers.

\( r_{ij} \)  Distance between the species \( i \) and \( j \).
Glossary

$\epsilon_{ij}$ Lennard-Jones interactions energy between the components $i$ and $j$ of the solution.

$\epsilon_{iw}$ Lennard-Jones interactions energy between the $i^{th}$ component of the solution with the charged surface.

$\Gamma$ The surface concentration of ionizable groups.

$\delta$ $\delta = 2\sqrt{K_-/K_+}$ for $K_-$ and $K_+$ are the dissociation constants of chemical equilibrium between the surface reactive groups and potential determining ions.

$d_s$ Diameter of solvent.

$h$ In theory this is used for reduced Planck’s constant. In chapter 6 and discussions with overlapping double layers, $h$ is used for wall separation distance.

$k_B$ Boltzmann Constant $1.3806488 \times 10^{-23} J/K$

$T$ Temperature of the system (always sued physiological temperature of 298.15K) throughout this manuscript.

$z$ Spatial Coordinate, usually distance from the surface into the solution.

PB Poisson-Boltzmann Constant.
Chapter 1

Introduction

1.1 Overview

Most materials, when brought in contact with water or any electrolyte, spontaneously ionize. A very familiar example is NaCl, which readily falls apart, splitting into Na\(^+\) and Cl\(^-\). Indeed, even so-called pure water by itself will see a small fraction of water molecules split into H\(_3\)O\(^+\) and OH\(^-\), thus giving rise to the concept of pH, and providing for a small electrical conductivity. Similarly, when a large molecule such as a protein or a solid surface such as silica is contacted by water, it will acquire a charge as a consequence of ionizable groups splitting off an ion. A relevant example is silica, SiO\(_2\), which has terminating hydroxyls, SiOH, which can split off a proton and leave a negative charge on the surface. This is the typical picture of electric double layer, where the charged surface exerts a potential across the surface leading to the spatial redistribution of ionic species in the solution.

Naturally, the chemical equilibrium is characterized by a change in Gibbs free energy or, equivalently, by an equilibrium constant, K. Often there exist multiple ways of leaving the surface charged. For example the hydroxyl, SiOH, may also bind
Chapter 1. Introduction

an available proton to pick up a positive charge, i.e.,

\[ \text{SiOH} \rightleftharpoons \text{SiO}^- + \text{H}^+ \quad \text{pK}_- = -\log_{10} K_- \]

\[ \text{SiOH}_2^+ \rightleftharpoons \text{SiOH} + \text{H}^+ \quad \text{pK}_+ = -\log_{10} K_+ . \]

Surfaces that can split off positive ions as well as bind positive ions are referred to as amphoteric surfaces. They can end up charged negatively or positively depending on the electrolyte conditions. Specifically, the final equilibrium charge depends on both equilibrium constants and the local concentration of the ions involved in the reactions, here \( \text{H}^+ \) (or \( \text{H}_3\text{O}^+ \)). The ions participating in the surface chemical reaction(s) are referred to potential determining ion(s) or PDIs.

In the example above, the final surface charge (as well as the final electric surface potential) depends on the constants \( K_+ \) and \( K_- \), temperature, \( T \), the pH and the concentration of any added salt. The added salt, NaCl, say, does not directly participate in the chemical surface reactions. However, the presence of added salt does, indirectly, affect the surface concentration of \( \text{H}^+ \) (or \( \text{H}_3\text{O}^+ \)) and hence it will shift the equilibria. The way the ions of the added salt affect the local proton concentration is through the local electric potential inside the so-called electric double layer (EDL).

In other words, changing the PDI concentration (here pH) will directly change the surface charge (and surface potential) because it changes the surface concentration. However, spectator species like non-PDIs (i.e., added salt) can also shift the surface equilibria by their effect on the EDL.

To put this in more general terms then, the surface charge (or surface potential) depends on the shift in equilibrium due to the environmental parameters (e.g., hydration, composition). For instance, in an experiment or in a modeling approach these parameters can be varied by manipulation of the solvent. Doing so changes the reaction free energy, through changes of the dissociated state of the PDIs and the ionized surface group on the one side of the reaction, and the non dissociated
Chapter 1. Introduction

This Doctoral dissertation presents a model of electric double layer with the above mentioned reactive surface that alters its surface charge based on the above chemical equilibrium between the potential determining ions in the solution with that of surface reactive groups. Does the structure of solvent affect electrostatic properties of EDL like the charge on surface and the distribution of ionic species? Do the non-electrostatic interactions like ionic solvation, solvent - solvent interactions and the interactions of ions and the solvent with the charged wall affect electrostatic properties of electric double layer? The above questions are addressed in the chapters 2-5 in this thesis. The theory, background and details about the computational model are given in chapter 1. Also, when the electrolyte solution is confined between the charged surfaces due to the excluded volume of solvent, structural forces develop. These also affect the charge distribution inside electric double layers of the confined electrolyte solutions. These are elucidated in detail in chapter 6 of this thesis.

1.2 Background and Motivation

Interfaces involving electrolyte solutions are common in nature as well as in various fields of fundamental and applied research. The contact surface between the electrolyte solution and the second phase is usually charged, leading to a spatial redistribution of ions historically known as an electric double layer (EDL). The surface charge is due to an externally applied potential in the case of metal electrode or to specific surface chemistry in the case of dielectric materials. The EDL is a key concept pertinent to important areas such as colloid and interface science, electrochemistry, corrosion, material science, etc. Therefore it is not surprising that EDLs have been extensively studied for more than a century and the efforts to obtain deeper insights continue at the present time. The first attempt to provide a physical
interpretation of the EDL was offered by Helmholtz [1], who considered the charge redistribution at the interface as a simple capacitor. Later it was realized that this is not an accurate representation because of the diffuse distribution of ions in the vicinity due to the thermal motion. A better model, proposed independently by Gouy [2] and Chapman [3], described the ionic distribution using a continuum approximation known as the Poisson-Boltzmann (PB) equation [4]

$$\nabla^2 \psi = -\frac{1}{\varepsilon \varepsilon_0} \sum_i \rho_i^0 q_i \exp \left( \frac{-q_i \psi}{k_B T} \right)$$  \hspace{1cm} (1.2)

where $\psi$ is the electrostatic potential, $q_i$ is the charge of ion species "i" (in units of the elementary charge $e$), $k_B T$ is the thermal energy, $\rho_i^0$ is the bulk number density of charged species $i$, $\varepsilon$ and $\varepsilon_0$ are the medium dielectric permittivity, and the dielectric constant of vacuum. The Gouy-Chapman approach does not explicitly account for the ionic size and associated correlations in the EDL, which is problematic near the charged interface. This issue was first addressed by Stern [5] and Graham [6] who suggested the presence of a finite sized layer of ions and solvent molecules adjacent to the surface. This layer acts as a capacitor in addition to the diffuse potential determined by the PB equation (3.1). The idea was further developed by other authors [7–11] who offered various modifications of the PB equation in an attempt to improve the description of the EDL.

More rigorous analyses of EDLs are based on modern statistical mechanics [12–14]. These approaches are usually based on the Ornstein-Zernike (OZ) integral equation or classical density functional theory (DFT) [15–20]. Often their implementation is limited to explicitly accounting only for the charged ionic species while the solvent is considered as a structureless continuum. Such models are referred to as "primitive", while a full inclusion of all species including the solvent defines a "civilized" model (this terminology is attributed to R. H. Stokes [21]). Both the primitive [22–28] and civilized [20,29–36] models are applied to study charged interfaces. Clearly, the civilized models are superior because they account for all species in the electrolyte so-
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olution. In fact, it was demonstrated that the primitive statistical mechanical models yield results that are identical to those obtained from solving the modified Poisson Boltzmann equation \[37\]. Hence a truly realistic description of charged interfaces that involve electrolytes requires a civilized model that explicitly acknowledges the explicit presence of the solvent molecules alongside all ionic species.

Another important aspect of EDLs is associated with the mechanism of surface charge formation. It usually originates from dissociation of surface groups, ionic adsorption from the solution bulk or both \[38\]. These details are lost when Eq. (3.1) is solved as Dirichlet or a Neumann boundary value problem where either the surface potential $\Psi_s$ or the surface charge $\sigma = -\varepsilon \varepsilon_0 (\nabla \Psi)_s$ are fixed at a constant value. This is not physically correct as pointed out by Ninham and Parsegian \[39\] who insisted that the boundary condition at the interface should reflect the thermodynamic equilibrium between the surface reactive groups and certain ionic species in the bulk referred to as potential determining ions (PDIs). This boundary condition is known as surface charge regulation (CR) and it presents a significant improvement in analyzing a variety of physical problems involving EDLs \[40\]-\[49\].

Until recently, the CR condition was not applied in conjunction with more elaborate statistical mechanical analysis of EDLs as those discussed above. An important step in that direction was taken by Heinen et al. \[28\], who applied the CR concept to a charged colloidal dispersion analyzed using the primitive (solvent excluded) OZ integral equation approach. The solvent effect in combination with CR boundary condition was first analyzed in our recent publication \[36\]. The analysis revealed that the surface CR condition strongly couples to the detailed solution structure in the immediate vicinity of the charged interface. This structure is dominated by the solvent because of its enormous concentration in comparison to that of the dissolved ions. The solvent molecules provide a structural matrix which determines the local ionic distribution. We have demonstrated that due the solvent effect the den-
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sity distribution for the ionic species is liquid-like despite the fact that their actual concentration is gas-like [36].

In this present chapter, an extensive analysis of the solvent impact on the properties of EDLs with surface charge regulation is presented. Our particular focus is mostly on effects that have a non-electrostatic origin. These effects are largely responsible for experimental observations as the Hofmeister series [50, 51], the well-known electrokinetic measurements of Tadros and Lyklema [52], or the more recent results on the interactions between surfaces [53–55].

1.3 Theory

The focus of our study is on charged interfaces that involve electrolyte solutions (see Fig. 1.1). Our model is civilized as it explicitly includes all solution components including the solvent. The charge and potential are dependent on the local distribution of all ionic species and the solvent clearly has an impact on it. Following the historical tradition we will refer to the physical interface between the charged interface and the electrolyte solution as the inner Helmholtz plane (IHP), the layer of ions and solvent molecules in the immediate vicinity to the charged interface as Stern layer, [5]. The midplane of the Stern layer defines the outer Helmholtz plane (OHP). There is another plane of interest that is located between the first layer of ions (and solvent molecules) in the immediate vicinity of the interface and the bulk solution. It is often assumed that this is the shear plane (SP) known from the theory of electrokinetic phenomena [38, 56–58]. Detailed molecular dynamics simulations have shown that indeed the stagnant layer thickness is usually of the order of ions or solvent molecular diameter [59–63]. Hence, an electrokinetic measurement [57] is relevant to the charge and potential at the SP, after the first layer of ions and solvent molecules near the wall.
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1.3.1 Density Functional Theory for Charged Interfaces

EDLs involve multicomponent solutions, containing charged (ionic) and neutral (solvent) species. These species are subjected to the effects of the field exerted by the interface with the substrate. The field has electrostatic and van der Waals components, which lead to a variety of interactions with the fluid. In addition, the solution components \((M)\) in the fluid interact with each other. All of these interactions are easily incorporated in a cDFT model.

The electrolyte solution is described in terms of a grand thermodynamic potential functional, which for single flat EDL reads, [15,16,20,36,64–66],

\[
\Omega \left[ \{ \rho_i(z) \} \right] = F_{id}^\varepsilon \left[ \{ \rho_i(z) \} \right] + F_{HS}^\varepsilon \left[ \{ \rho_i(z) \} \right] + F_{long}^\varepsilon \left[ \{ \rho_i(z) \} \right] + \\
2\pi \sum_{i=1}^{M} \int dR \int \mathcal{R} d\mathcal{R} \int dz \rho_i(\mathcal{R},z) \left[ V_i^{ext}(\mathcal{R},z) - \mu_i \right]. \quad (1.3)
\]
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The first term on the right hand side of Eq. (1.3) corresponds to the ideal contribution to the free energy,

\[
F^{id}[[\rho_i(z)]] = 2\pi k_B T \sum_{i=1}^{M} \int \mathcal{R} d\mathcal{R} \times \int dz \rho_i(\mathcal{R}, z) \left\{ \ln \left[ \lambda_i^3 \rho_i(\mathcal{R}, z) \right] - 1 \right\},
\]

where \( \lambda = \sqrt{\hbar^2/(2\pi m_i k_B T)} \) is the thermal de Broglie wavelength, \( \hbar \) is Planck’s constant, \( m_i \) is the mass of species “\( i \)”, and \( \rho_i(z) \) is the local density of component “\( i \)” along the \( z \) coordinate normal to the wall. The radial coordinate \( \mathcal{R} \) runs parallel to the EDL interface with the substrate.

The excess free energy consists of hard-sphere and long-range parts. The hard-sphere contribution is based on the derivation of Rosenfeld [18,19] and reads

\[
F^{ex}_{HS}[[\rho_i(z)]] = 2\pi k_B T \int \mathcal{R} d\mathcal{R} \int dz \Phi_{HS} \left\{ n_\alpha(\mathcal{R}, z) \right\}.
\]

\( \Phi_{HS} \{ n_\alpha(\mathcal{R}, z) \} \) is the hard-sphere reduced free energy and \( n_\alpha(\mathcal{R}, z') = n_\alpha(r) \) (\( r \) being the position vector) is the weighted local density.

\[
\Phi_{HS} \{ n_\alpha(r) \} = -n_0 \log(1 - n_3) + \frac{n_1 n_2 - n_1 \cdot n_2}{1 - n_3} + \frac{n_3^2 - 3n_2 n_2 \cdot n_2}{24(1 - n_3)^2}.
\]

Remarkably, the functional form of the reduced free energy \( \Phi_{HS} \{ n_\alpha(\mathcal{R}, z) \} \) is independent on the number components \( M \). It is the weighted densities \( n_\alpha(r) \) exhibit such a dependence and are defined by

\[
n_\alpha(r) = \sum_{i=1}^{M} \int d^3r' \rho_i(r') \omega_\alpha^i(r - r'),
\]

and the weighting functions \( \omega_\alpha^i(r) \) are

\[
\omega_3^i(r) = \Theta(R_i - r), \quad \omega_2^i(r) = \delta(R_i - r),
\]

\[
\omega_1^i(r) = \frac{\omega_2^i(r)}{4\pi R_i^2}, \quad \omega_0^i(r) = \frac{\omega_2^i(r)}{4\pi R_i^2},
\]

\[
\omega_2^i(r) = \frac{r}{r} \Theta(R_i - r), \quad \omega_1^i(r) = \frac{\omega_2^i(r)}{4\pi r_i}.
\]
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The long-range contribution to the free energy functional is

\[
F_{\text{long}}^{\text{ex}}[\{\rho_i(z)\}] = \frac{\pi}{2} \sum_{i=1}^{M} \sum_{j=1}^{M} \int R dR \int dz \times \int dz' \rho_i(R, z) \rho_j(R, z') \Phi_{LR}(R, |z - z'|), \quad (1.11)
\]

where \(\Phi_{LR}(R, |z - z'|)\) is the long-range interactions contribution of the reduced free energy. Eq. (1.11) indicates that the long range interactions are accounted for in a mean-field limit. \(67\)

The last term in Eq. (1.3) is the Lagrangian constraint, which accounts for the external fields \(V_i^{\text{ext}}\) and fixed chemical potentials \(\mu_i\) for all species.

The equilibrium density profiles of all components \(\rho_i(z)\) are found by minimizing the functional, \(68\)

\[
\frac{\delta \Omega[\{\rho_i(z)\}]}{\delta \rho_i(z)} = 0. \quad (1.12)
\]

The charge density distribution in the EDL is derived by summing over the individual charged species, taking into account the charge numbers with their sign

\[
\rho_e(z) = \sum_{i=1}^{M} q_i \rho_i(z). \quad (1.13)
\]

This approach includes the contributions of the interactions between the solutions species, which are present in the terms \(F_{H}^{\text{ex}}[\{\rho_i(z)\}], \quad 18,19\) which accounts for the excluded volume effects, and \(F_{\text{long}}^{\text{ex}}[\{\rho_i(z)\}],\) which captures long-range interactions. In our model, these interactions are of the Lennard-Jones (LJ) \(69\)

\[
\Phi_{\text{LJ}}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{d_{ij}}{r_{ij}} \right)^{12} - \left( \frac{d_{ij}}{r_{ij}} \right)^{6} \right], r_{ij} > d_{ij} \quad (1.14)
\]

and Coulombic

\[
\Phi_{\text{el}}(r_{ij}) = \frac{q_i q_j e^2}{4\pi \varepsilon \varepsilon_0 r_{ij}^2}, r_{ij} > d_{ij}, \quad (1.15)
\]
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type \[20,36,64–66\] where \(d_{ij} = (d_i + d_j)/2\), \(d_i\) is the diameter of component “i”, and \(r_{ij}(R, z)\) is the distance between species “i” and “j”. All non-Coulombic interactions of a molecule (or ion) of type “i” with the surface are assumed to be of the “hard wall” type, i.e. only the excluded volume effects are taken into account. The only exception is our analysis of the solvent-wall interactions presented in Section 3.3 below, where the LJ (9-3) potential [69]

\[
\Phi_{LJ}(z) = \epsilon_{s-w} \left[ \frac{2}{15} \left( \frac{d_s}{z} \right)^9 - \left( \frac{d_s}{z} \right)^3 \right], \quad z > d_s/2
\]  

(1.16)
is used in the analysis. The electrostatic interaction of the ions with the interface is

\[
\Phi_{el}(z) = \frac{q_i \sigma z}{2\varepsilon \varepsilon_0}, \quad z > d_i/2.
\]  

(1.17)

Using a solution model based on a combination of Coulombic and LJ interactions is clearly an approximation when polar or polarizable solvents (i.e., water) are involved. Nevertheless, it captures important features of electrolyte solutions, such as attractive and repulsive interactions between all solution components. [36]

This approximation works reasonably well for low to moderate ionic concentrations. [21, 30, 64, 70, 71] In such cases, the average distance between the charged species is sufficiently large so that any ion-induced local perturbation of the solvent molecular structure relaxes to the bulk state before reaching another ion [72]. For example in our case, the overall ionic concentration corresponds to 0.01 M. Assuming that the solvent molarity is 55.5 M, the average distance between two ions is \(\sim 30\) solvent molecular diameters. Even close to the charged surface, where the ion densities are greater (see Figure 1 below), the distance separating two ions is \(\sim 10\) molecular diameters. As Carnie and Chan [43] showed, the local polarization perturbation decay to the bulk value over distances of the order of 3-4 molecular diameters. The overall free energy may also be reduced due to local polarization response of the solvent near the charged interface. We can mimic that effect by varying
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the solvent-wall interaction. While empirical and therefore not ideal, this approach has the advantage of being considerably simpler and computationally efficient.

The Coulombic interactions are included in $F_{\text{long}}^\text{ex}(|\rho_i(z)|)$ [see Eq. (1.11)], and are therefore treated within a mean-field approximation. cDFT allows to include higher order correlations that are beyond the electrostatic mean-field approximation, but they lead to noticeable contributions at much higher ionic concentrations [73].

1.3.2 Charge Regulation at the Surface Boundary of an Electric Double Layer

The chemistry responsible for the charging of surfaces in contact with electrolyte solutions can be very complex involving a multitude of possible reactions [40]. We use a relatively simple yet sufficiently comprehensive model suggested by Chan et al. [43], which involves two surface reactions

\begin{align}
\text{AH}_2^+ + \text{BH} & \rightleftharpoons \text{AH} + \text{BH}_2^+, \quad \text{pK}_+ = -\log_{10} K_+ \\
\text{AH} + \text{BH} & \rightleftharpoons \text{A}^- + \text{BH}_2^+, \quad \text{pK}_- = -\log_{10} K_-
\end{align}

where $K_+$ and $K_-$ are the equilibrium constants, and AH is a surface chemical group that can either bind or release a proton depending on local densities $\rho_{\text{BH}_2^+}$, $\rho_{\text{BH}}$ of species $\text{BH}_2^+$ and BH in the solution. The species BH can split according to the bulk reaction

\begin{align}
2\text{BH} & \rightleftharpoons \text{B}^- + \text{BH}_2^+
\end{align}

and produce a pair negative and positive ions. The positive species $\text{B}_2^+$ is the PDI and it is its subsurface layer concentration that is involved in the equilibrium (1.18). The negative ions $\text{B}^-$ are natural counterions of the PDIs. In addition, there are also negative ions that are introduced as counterions of the non-PDIs (i.e., the background
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electrolyte). They do not participate in the reaction (1.19) but are otherwise taken to be identical in terms of size, charge and all LJ interactions to B$^-$. Therefore, in the discussion below we will not discriminate between the types of negative ions that are present in the solution and will consider them as single species.

A proper account for the concentration of species in the subsurface (i.e. Stern) layer is very important. It determines the local concentration of each component and in the case of PDIs has an effect on the equilibria (1.18), and on the resulting surface charge at the IHP. Since all solution species have finite size, we determine this concentration using {see Supplemental Material in Ref. [36]}

$$\rho_s^i = \frac{\int_{0}^{d_i/2} dz \rho_i(z)}{\int_{0}^{d_i/2} dz}.$$ (1.20)

The surface charge then reads [43]

$$\sigma = e\Gamma \frac{\rho_{A\mathrm{H}_2}^s - \rho_A^s}{\rho_{A\mathrm{H}_2}^s + \rho_{A\mathrm{H}_2}^s + \rho_A^s}$$

$$= e\Gamma \frac{\delta \sinh[e(\Psi_N - \Psi_s)/k_B T]}{1 + \delta \cosh[e(\Psi_N - \Psi_s)/k_B T]}.$$ (1.21)

where $\delta = 2\sqrt{K_-/K_+}$, $\Gamma$ is the surface concentration of ionizable groups, and $\Psi_s$ is the surface potential. The quantity $\Psi_N = [\ln(10)k_B T/e] (\text{pI} - \text{pH}_b)$ is the Nernst potential where $\text{pI} = (\text{pK}_- + \text{pK}_+)/2$ is the surface isoelectric point and $\text{pH}_b$ is the pH value in the bulk solution, far from the charged interface. The relationship (1.21) corresponds to a measurement of the surface charge using the titration method mentioned above.

Finding the density distributions of all ionic species in the solution allows for determining the overall charge density distribution

$$\rho_e(z) = \sum_{i=1}^{M} q_i \rho_i(z)$$ (1.22)
more accurately than using the approximate Eq. (3.2). The charge density can be then introduced in Eq. (3.1) to find the electrostatic potential distribution in the solution, and at the surface.

The surface charge is also equal (and opposite in sign) to the net bulk charge, or

\[
\sigma = -\sum_{i=1}^{M} \int_{0}^{\infty} q_i \rho_i(z) dz
\]

(1.23)

where \( M \) is the total number of components in the solution. Since the solvent is neutral, it is formally treated as a component with zero charge \( (q_s = 0) \).

Eqs. (3.1), (1.21), (1.22), and (1.23) are then iteratively solved to obtain the surface charges and potentials, as well as the corresponding distributions in the fluid phase.

The computations are performed using the free-ware Tramonto code\cite{74} to minimize the grand thermodynamic functional [see Eq. (1.12)]. The parameters governing the surface chemistry are \( \Gamma d^2/e = 0.66 \), pH = 4, \( \mathrm{pK}_- = 6 \), and \( \mathrm{pK}_+ = -2 \).\cite{36,64,75} The ionic strength is 0.01 M. The solvation energy was varied between 0 and \( 1.2k_B T \) to avoid numerical stability problems when approaching the triple point for LJ fluid, which is around \( \sim 1.4k_B T \).\cite{76}

The boundary condition for the surface charge is given by Eq. (1.21). The densities far away from the interface are equal to their fixed bulk values. The number of surface ionizable groups for both cases is assumed to be \( \Gamma = 8 \times 10^{18} \text{m}^{-2} \). If fully ionized, this number leads to a dimensionless surface charge density \( \sigma d^2/e = \pm 0.664 \). The length-scale \( d \) corresponds to a characteristic molecular (or ionic) diameter. It is set to \( d = 0.288 \text{nm} \), which ensures that for a reduced liquid density \( \rho d^3 = 0.8 \), the molarity is 55.5 M.

All above parameters were selected because they are within the typical range for common oxides like SiO\(_2\) and Al\(_2\)O\(_3\) respectively\cite{77}. The bulk pH = 4 for the
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solution in contact with SiO$_2$ and pH = 5 for Al$_2$O$_3$. These were selected in order to provide examples for negative and positive surfaces, while being relevant to realistic situations.
Chapter 2

Effect of electrolyte solution structure on the properties of EDL

2.0.1 Solution Structure and Its Effect on the Surface Charge

The precise structure of an electrolyte solution strongly couples to the surface chemistry [see Eq. (1.18)], and therefore plays an important role in determining the surface charge [36]. Here we expand the analysis and present data that provide further insights into the physics underlying this observation. The effect of the solvent molecular structure can clearly be demonstrated by examining the dependence of the surface charge on the size of the solvent molecules. Varying that size from zero to a finite value (e.g., same as the size of the ions in the solution) is equivalent to gradually "turning on" the solvent contribution to the structure with all the excluded volume and attractive interactions that follow from it. We present two cases that correspond to (i) pI = 2, ΔpK = 8, and (ii) pI = 8, ΔpK = 4, where ΔpK = pK_ - pK_+ (see Fig. 2.1). More details are provided in the previous chapter.
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Figure 2.1. Surface charge of an EDL as a function of the solvent molecular diameter. The different curves are for different values of the LJ parameter $\epsilon_{ij}$, which starts at zero (top curve) and increases by increments of $0.1 \ k_BT$, with the exception of the dashed curve, which is for $\epsilon_{ij}/k_BT = 0.76$ (see the text). The dot corresponds to the critical point. (a) $pI = 2, \Delta pK = 8$ and $pH = 4$. (b) $pI = 8, \Delta pK = 4$ and $pH = 5$.

Fig. 2.1 demonstrates the effect of the solvent structure and LJ attraction on the resultant dimensionless surface charge $\sigma d^2/e$, according to the chemical equilibrium (1.18). Only bulk LJ interactions are included. The LJ interactions of all solvent...
component with the wall are considered to be zero. The wall however is hard and impenetrable and its surface charge generates an electric potential that affects the distributions of all ions in the EDL. Fig. 2a corresponds to $pI = 2$, $\Delta pK = 8$ and $pH = 4$ and Fig. 2.1b to $pI = 8$, $\Delta pK = 4$ and $pH = 5$. The solution ionic strength (including all ionic contributions) is equal to 0.01M. As the attraction increases (in steps of $\Delta \epsilon_{ij}/k_BT = 0.1$), the trend of increasing the surface charge $\sigma$ with $d_s/d$ becomes weaker and non-monotonic. The surface charge dependence on the solvent diameter is very strong when the latter approaches those of the ions ($d_s/d \rightarrow 1$). This means that small variations in the relative dimensions have a significant effect on the surface charge. The surface charge depends on the equilibrium between the surface reactive groups and the PDIs in the stern layer. The repulsive interactions involving the PDIs in the bulk will shift the equilibrium in favor of reducing the surface charge magnitude because the free energy will drop as the ions move from the bulk towards the interface. On the other hand, increasing the attractive bulk interactions with the solvent (e.g., solvation) will have the opposite effect on the free energy and thus will favor an increase in the surface charge.

The increase of the solvent diameter in Fig. 2.1 is formally equivalent to increasing the liquid density, and in presence of attractions this lead to liquid-vapor phase separation, which is indicated in the figures by the dashed lines. These correspond to the spinodal lines and depict the domains of thermodynamic instability. The behavior at $d_s \rightarrow 0$ is not realistic because it also corresponds to a systems of very low gas-like density. The more realistic civilized analysis corresponds to the far right side of the figure. Clearly any analysis that ignores the solvent correlation misses a number of physical effects and is therefore incomplete. However, a proper account of the solvent molecular structure alone is not sufficient if the surface charge regulation condition (1.18) is replaced by constant surface potential or constant surface charge boundary condition. This wide variety of physical effects is due to the coupling between the surface charge regulation and the complete solution structure. Examining
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Fig. 2.1, it is clear that using a primitive electrolyte model to describe EDLs suffers similar shortcomings as the application of the ideal gas equation of state to dense liquids.

![Graph](image_url)

Figure 2.2. Density distribution for ions and solvent in the vicinity of a negatively charged interface $p_I = 2, \Delta pK = 8$ and $pH = 4$, in absence of attractive LJ interactions. The top curve is for the PDIs and positive non-PDIs, which follow exactly the same trend. The middle curve corresponds to the density of the solvent molecules and the bottom curve is for the negative ions. The smooth dashed curves depict the primitive model solution. The inset shows the structural effect. Peak height exhibits an exponential decay – see the text for more details.

The cases depicted in Figs 2a and 2b are similar in some aspects and quite different in others. The common features were outlined above and here we discuss the differences. Fig. 2.1a is for a relatively weakly negatively charged surface, while Fig. 2.1b is for a positive surface and the charge magnitude is greater. This leads to a noticeably different behavior near the limit of vanishing solvent molecular size, which is the domain of the primitive model. As the solvent diameter goes to zero all curves in Fig. 2.1a collapse onto the same value for the surface charge. In Fig. 2b the curves intercept the vertical axis at different values for the surface charge. The reason for that is because the higher surface charge magnitude (in comparison with
Fig. 2a) attracts a greater number of counterions (negative in this case) and the inter-ionic correlations are present. It is to be noted that the primitive model, the solvent correlations are not taken into account. However, all ions participate in the model with their physical size and interactions. The absence of explicit solvent in the model leads to an overestimate of the ionic local concentrations and correlations in the vicinity of the charged interface. These correlations are dependent on the LJ interactions, which leads to the variations in the surface charge observed in the limit of \( d_s \rightarrow 0 \). Interestingly, as the solvent structural contribution increases, it seems to offset the ion-ion correlation induced variations and completely eliminate them around \( d_s/d \simeq 0.3 \). After that point the curves for various LJ parameters \( \epsilon_{ij} \) diverge from one another again as \( d_s/d \rightarrow 1 \). Another important difference between the two figures is that the critical point in Fig. 2b is shifted towards slightly higher attractive LJ energy \( \epsilon_{ij}/k_B T \simeq 0.8 \) instead of 0.76). This observation can also be attributed to the greater ionic concentration in the EDL due to the more significant surface charge magnitude (compared to the case in Fig. 2a). Most of the ions in the EDL have the same charge (opposite to that of the interface) and hence repel each other. As a result, it requires more attractive energy to bring them closer into a liquid state.

In our earlier work \[36\], we have found that there are two characteristic lengths associated with the EDLs. One is the well known Debye screening length \((\kappa^{-1})\) \[78\]

\[
\kappa = \left( \frac{1}{\varepsilon \varepsilon_0 k_B T} \sum_i \rho_i^0 q_i^2 \right)^{1/2}
\]  

where \( \rho_i^0 \) is the bulk concentration of species \( i \). Fig. 2.2 presents data for the density distribution of all species in the vicinity of the charged interface. The first and highest peak corresponds to the Stern layer, while the minimum after it defines the location of the SP (see Fig. 1.1). A second characteristic length is a measure of the structural
effects and their decay with the distance from the charge surface. Following the work of Martynov [79], we analyzed the peak heights of the local density distribution after subtracting all long-range contributions such as Coulombic or LJ interactions (see Fig. 2.2). The reduced density then is defined as $\rho_{\text{reduced}} = \rho_{\text{DFT}} - \rho_{\text{PB}}$, where the subscript DFT and PB refer to a civilized density functional and continuum Poisson-Boltzmann solution respectively. In this case, all density distribution curves collapse onto a single one and its peak heights values decrease exponentially, i.e. $\sim \exp(-\beta z)$. The decay length associated with the decrease is $\beta = 1.3d$ (assuming that all species have the same size) [36].

### 2.0.2 Effects of the Surface Chemistry.

The charge at the interface between the electrolyte solution and the other phase (i.e., the IHP) is governed by the reaction equilibria (1.18), which in turn is characterized by the equilibrium constants, or equivalently by the values of $pK_+$ and $pK_-$. These parameters determine how the surface groups will respond to the local concentration of the PDIs. The latter is determined by the value of the pH. Fig. 2.3 shows the results for two different EDL systems. Fig. 2.3a corresponds to a surface isoelectric point $pI = 2$ and Fig. 2.3b to $pI = 5$. The total concentration of electrolyte is 0.01 M, therefore the lower limit on the horizontal axis is pH = 2. The different curves in both panels reflect the specific surface chemistry in terms of the value of the parameter $\Delta pK = 2, 4, 6, 8, 10, \text{ and } 12$. The smaller $\Delta pK$ the more responsive the surface is to pH variations (see also Ref. [46]). Hence, the magnitude of the surface charge depends on the surface $pI$, the solution pH and the parameter $\Delta pK$. Larger differences between the $pI$ and pH, lead to greater magnitudes of surface charge. The overall behavior of charge regulating surfaces described above, is qualitatively consistent with experimental observations (see for example Ref. [52]). The actual isoelectric point for $pI = 5$ (see Fig. 2.3b) is slightly shifted to a higher value, which
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Figure 2.3. Surface charge of an EDL as a function of the solvent pH (i.e. the concentration of PDIs). The different curves are for $\Delta pK = 2, 4, 6, 8, 10, 12$. The smaller $\Delta pK$, the steeper the curves. (a) pI = 2; (b) pI = 5.

is due to the effect of the finite size of all participants. In the charge regulation model that we use, the equilibrium constants [see Eq. (1.18)] do not explicitly account for the any effects due to the molecular size of the solution species. This effects are added with the implementation of the civilized DFT approach and lead to the observed shift.
2.0.3 Effects of the Bulk Ionic Strength.

![Graph showing surface charge of an EDL as a function of the solution ionic strength in moles per liter.](image)

Figure 2.4. Surface charge of an EDL as a function of the solution ionic strength in moles per liter. pH = 2, ΔpK = 8 and pH = 4. (a) Charge at the actual interface; (b) Charge at the outer boundary of the Stern layer.

The total bulk electrolyte concentration (i.e., ionic strength) modifies the potential distribution in the EDL through screening. Hence, it affects the potential at the surface, which in turn reflects on the surface charge [see Eq. (1.21)]. Figure 2.4 illus-
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trates the effect of the total bulk electrolyte concentration in terms of ionic strength \( I = \frac{1}{2} \sum z_i^2 C_i \). The ionic strength includes the molar concentrations \( C_i \) of all ionic species, including the contributions of the PDIs, which depend on the solution pH. The surface charge at three different pH values are analyzed. The pH effect is obvious and it is due to the chemical equilibria (1.18) [see also (1.21)]. The decrease of the surface charge with the bulk concentration of non-PDIs is a result of the overall charge and potential modification that stems from bulk charge screening. It modifies the overall potential distribution in the EDL as well as the surface potential \( \Psi_s \) [see (1.21)].

Fig. 2.4a shows the charge at the IHP and Fig. 2.4b corresponds to the charge at the SP. The values for the surface charges in these two cases are very different since the net charge of the Stern layer is effectively subtracted from the charge due to actual ionization of the surface. This is in general qualitative agreement with experimental observations [80–83] which predict a charge variation with the pH of the solution.

2.1 Conclusions

The charge formation at electrolyte interfaces and the properties of EDLs are complex functions of many parameters related to the material properties of the surface and the adjacent solution. The interfacial charge at the IHP is determined by surface chemical reactions (charge regulation) involving the surface reactive groups and components of the solution. All solution components contribute to the final surface equilibria, including species that are not directly participating in the surface reactions, (1.18). We also show in the following chapters that the precise and detailed solution structure in the vicinity of the interface couples to the charge governing chemical equilibria. The solvent molecules play an important role in establishing
this structure due to their exceedingly large number. The solvent contributes to the ionic structure through the excluded volume and LJ interactions. Hence, an accurate physical representation of charged interfaces involving electrolytes requires rigorous statistical mechanical approaches that explicitly account for all solution species and the correlations among them.

The surface chemistry plays an important role for the charge regulating behavior in EDLs. It depends on the material properties of the interface and the composition of the electrolyte solution in contact with it. This is governed by three parameters: the pI of the surface, the bulk concentration of PDIs (in case of hydronium ions this is conveniently expressed by the pH), and the difference $\Delta pK = pK_+ - pK_-$.

The analysis also asserts that the properties of an EDL with surface charge regulation strongly depends on non-Coulombic interactions and correlations in the electrolyte solution. Examples include the bulk solvation as well as non-electrostatic interactions with the EDL interface. The analysis of the solvation and surface interactions explains the fact that different types ions carrying the same charge may lead to a different outcome for the resultant surface charge. It also explains why components that are not directly involved in the surface chemical reactions affect the EDL properties. Hence, the combination of solvation and surface interactions can account for experimental observations that lead to the definition of the Hofmeister series [50, 51], electrokinetic results [52], or the ions-specific surfaces forces [53–55].

An important aspect of this study is to provide a framework for proper analysis of experimental data. As discussed above depending on the method one may directly probe the charge at the surface by counting the number of charged groups (using titration) or detect the charge at the shear plane (using electrokinetic methods). These could be and often are very different. Civilized DFT allows to distinguish between these cases and provides an explanation for the difference based on rigorous
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statistical mechanical arguments.

The main focus of this study is on the properties of static EDLs. However, DFT can be generalized to non-equilibrium systems [17, 84]. This will allow solving problems pertinent to surface reactions and solute diffusion.

In summary we believe that civilized statistical mechanical approaches (such as DFT) together with a proper account for all chemical equilibria at the EDL boundary offers the best theoretical background for modeling and analysis of charged interfaces that involve electrolyte solutions. The simple model presented in this work can be extended to include more components and/or more sophisticated functionals. This is a strategy that allows obtaining further insights into the properties of charged colloidal systems.
Chapter 3

Ionic Solvation and Solvent-Solvent interactions effect on EDL

3.1 Introduction

Anything that changes the free energy difference between the reactants and products will potentially lead to a change in the surface quantities (i.e., charge or potential). Heterogeneous regions such as interfaces and EDLs are prime examples of this phenomenon. As we have shown in a series of papers [36, 64] on EDL phenomena, classical Density Functional Theory (cDFT) is uniquely suited for an investigation of this sort. cDFT minimizes a free energy functional and is firmly anchored in statistical mechanics and, at equilibrium, provides direct access to the free energy. In addition, our cDFT calculations explicitly represent the solvent as atoms. Given that the number of solvent atoms greatly exceeds that of the ions, the solvent structure dictates the short-range structure of the EDL. [29, 34, 36, 64] Interestingly, even though the density profile of the net local charge distribution is strongly oscillatory,
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the electric potential, $\Psi$ is not. The Poisson equation \[4\]

$$\nabla^2 \Psi = -\frac{\rho_e}{\varepsilon \varepsilon_0},$$

is, of course, satisfied, guaranteeing that the second spatial derivative of $\Psi$ is proportional to the net local charge profile. But this does not preclude a monotonic $\Psi$, similar to what is found in a simple Poisson-Boltzmann approach \[2,3,85\] where

$$\rho_e = \sum_i \rho_i^0 q_i \exp \left(\frac{-q_i \Psi}{k_B T}\right).$$

where $\rho_i^0$ is the density of ionic species $i$ infinitely far from the interface, $q_i$ is the ion charge, and $k_B T$ is the thermal energy. Other parameters include the dielectric constant of vacuum $\varepsilon_0$ and the relative dielectric permittivity of the solvent phase $\varepsilon$.

In this chapter we explore the role of the solvation (hydration) interactions. We do this by varying the strength of the non-Coulombic interactions within the solvent as well as between the solvent and the ionic species. We examine the detailed charge and potential distribution in the bulk in the vicinity of charged interface. This includes the so-called Stern layer \[5\] and beyond, where the charge distribution is mostly diffuse.

### 3.1.1 Effect of the Bulk Solvation Interactions on surface charge and charge of stern plane

Interactions in the bulk of the solution compete with those with the surface. Since the solvent molecules are in overwhelming number, their interaction with the ionic species or among themselves will dominate. The importance of such analysis follows from the experimental fact that ionic solvation varies substantially from one species to another. For example, moving down the alkali column in the periodic table shows that the ions become less prone to water solvation \[86\].
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The surface charges in the present analysis are obtained at two locations: the physical interface (IHP) and after the first layer of ions, i.e. the SP (see Fig. 3.1). We examine the effect of the solvent LJ interactions [i.e., the parameter \( \epsilon_{ij} \) – see Eq. (1.14)] with each component: solvent-PDIs (solid curves), solvent-positive non-PDIs (dashed curves), solvent-negative ions (dotted curves) and solvent-solvent (dashed-dotted curves). Each curve was calculated while all other LJ interactions were set to \( \epsilon_{ij}/k_B T = 1 \). This is the reason why all curves intersect at that point. The remaining parameters are the same as in Fig. 2.1a.

Fig. 3.1a shows the effect of the bulk solvation interactions for all species on the charge at the IHP. If the PDIs (solid curve) are not too solvated they accumulate near the surface and neutralize the negative charges according to the reaction (1.18). However, as the solvent-PDI attraction increases the PDIs move away from the surface in the bulk, which naturally increases, the negative charge at the interface. The effect of the PDIs on the charge at the SP seems to follow the same trend as the one at the IHP (see the full curve in Fig. 3.1b). As the PDIs get more solvated the electrokinetic charge at the SP becomes more negative.

The solvation of the positive non-PDIs has a strong impact on the surface charge at the IHP (see the dashed curve in Fig. 3.1a). The charge magnitude at the IHP decreases with the increase of the solvation of the positive non-PDIs. Low solvation of the positive non-PDIs leads to increased accumulation near the interface, which in turn creates a repulsive electrostatic barrier for the positive PDIs to approach the interface thus reducing their concentration in the Stern layer. As a result the equilibrium (1.18) shifts towards a larger number of negatively charged surface groups A\(^-\). Increasing the solvation interactions favors a reduction of the concentration of non-PDIs in Stern layer and thus allows for a greater number of PDIs to reach the charged surface and neutralize some of the charged surface groups.

The effect of the non-PDIs on the charge at the SP however, is very different. If
the non-PDIs are not (or very weakly) solvated they tend to accumulate near the surface in the Stern layer. The latter becomes predominantly positive, which leads to an overall positive charge at the SP. As the solvation of the non-PDIs becomes
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stronger, they tend to leave the Stern layer, which results in more negative charge at the SP.

The solvent-solvent interaction seems to have a very similar effect on the charge both at the IHP (see the dot-dashed line in Fig. 3.1a) and the SP (dot-dashed line in Fig. 3.1b). A low LJ interaction between the solvent molecules leads to their preferential attraction to the rest of the species (including the PDIs, and non-PDIs) and facilitates their removal from the surface. As a result the local concentration of the positive PDIs and non-PDIs near the charged interface is low and the surface carries a highly negative charge. As the attraction between the solvent molecules increases, they will tend to maximize contacts with each other and minimize those with the PDIs. Hence, the PDI concentration near the charged interface decreases and the negative charge is reduced according the surface equilibria (1.18). Similarly, the non-PDIs numbers near the interface is reduced leading to their lower concentration in the Stern layer, which in turn determines the charge at the SP.

The solvation of the negative ions also affects the charges at the IHP and SP. The magnitude of the negative surface charge at the IHP (see the dotted line in Fig. 3.1a) slightly increases with the solvation of the negative ions. The reason for that effect is also in the electrostatic interactions with the PDIs. Larger numbers of negative ions near the surface attract the positive PDIs, thus reducing the surface charge according to Eq. (1.18). The charge at the SP on the other hand depends on the balance between the charges at the IHP and those in the Stern layer. Fig. 3.1b shows that the SP charge becomes less negative as the negative ions become more solvated. This is due to the reduction of the negative charges in the Stern layer, and hence results in lower overall negative charge at the SP.

The solvation interactions, while non-electrostatic in nature, have a very strong effect on the properties of charged interfaces that involve electrolytes. Hence, they allow to qualitatively explain why ionic species with same charge numbers may lead
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to different surface charge, or why different experiments (e.g., surface charge titration and electrokinetic measurements) may lead to different results.

3.1.2 Composition of the Stern layer

Figure 3.2. Mole fraction of solution components as a function of the solvation interaction of various species. The different lines correspond to PDIs (solid line), positive non-PDIs (dashed line), negative ions (dotted line), and solvent (dot-dashed line). (a) Solvent-solvent; (b) Solvent-PDIs; (c) Solvent-positive non-PDIs; (d) Solvent-negative non-PDIs.

Stern’s model [5] considers the finite size and specific interactions with the wall exhibited by the ionic species in this layer, but the rest of the EDL is still regarded as
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a continuum. cDFT is a major improvement in comparison with Stern’s approach, because it takes into account molecular and ionic correlations everywhere in the system. Still, the Stern layer defines an important sub-domain of the EDL. It is the layer, which is primarily involved in any chemical interactions with the surface. These could be instances of electrochemical charge transfer, or reactions that establish the surface charge such as Eq. (1.19). The physical dimensions of the Stern layer are also related to the position of the shear plane in electrokinetic phenomena. [59–63] Therefore, it deserves a more rigorous analysis.

The mole fraction of a component is calculated from the density profiles. If \( \rho_{st}^i \) is the density of a component in the stern layer, \( L \) is the thickness of stern layer, which is taken after the first minimum of density profiles

\[
\rho_{st}^i = \int_0^L dz \rho_i(z)/L. \tag{3.3}
\]

The mole fraction \( x_i \) of component \( i \) is given by

\[
x_i = \frac{\rho_{st}^i}{\sum_{i=1}^M \rho_{st}^i}. \tag{3.4}
\]

Fig. 4.2 demonstrates the mole composition in the Stern layer as a function of the solvation interaction for the different solution species. The solvation interactions are separately varied for the solvent, PDIs, positive and negative ions by varying the respective LJ energy [i.e., the parameter \( \epsilon_{ij} \) in Eq. (1.14)]. While the LJ parameter for a given component and the solvent is varied, the rest of the LJ interactions are maintained at 1 \( k_B T \).

It is immediately obvious the solvent is the dominant species in all cases. Also, the mole fraction of PDIs is consistently low. This is because the overall concentration of PDIs at pH = 4 is low in comparison with the rest of the species. Fig. 4.2b shows the effect of the solvent-solvent molecular, non-Coulombic LJ interactions on the
properties of the EDL. The relative change in the mole fraction of solvent with the LJ parameter $\epsilon_{s-s}$ is rather insignificant. The effects on the ions, however, are more noticeable. As the solvent molecules become more attracted to each other, they are less involved in solvation interactions with the ions. Hence, all ionic species tend to move from the bulk of the solution towards the interface and in the Stern layer. The mole fraction of positive non-PDIs exceeds that of the negative. This is due to the negative surface charge, which attracts the positive and repels the negative ions. The amount of PDIs also increases, which reduces the surface charge [see Eq. (1.19)].

Fig. 4.2b depicts the effect of the solvation interactions for the PDIs. As the PDI become more solvated ($\epsilon_{s-PDI}$ increases), their concentration in the Stern layer decreases. The reduction of the PDIs number in the Stern layer, leads to an increase in the surface charge because of a shift in the chemical equilibrium (1.19). The effect of the PDI solvation on the mole fraction of the positive and negative non-PDIs is primarily driven by the electrostatic interactions with the interface. As the charge increases the positive ions are attracted into the Stern layer, while the negative are repelled. The mole fraction of the solvent still dominates the composition of the Stern layer. Interestingly it passes through a slight maximum as the solvation interaction for the PDIs varies. This is most likely and excluded volume effect that stems from competition with the positive and negative ionic species.

Fig. 4.2c shows the effect of the positive non-PDIs solvation on the composition of the Stern layer. The greater solvation energy of the positive ions, $\epsilon_{s-pos}$, reduces their number in the Stern layer. This leads to an increase in the concentration of PDIs, which have less competition (in terms both excluded volume and Coulombic repulsion) to accumulate in the Stern layer. Their increase again affects the surface equilibrium (1.19). Some of the negative ions also transfer into the bulk to ensure overall bulk neutrality together with the positive ones.

Fig. 4.2d shows the effect of the solvation interactions for the negative ions.
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Following a trend, similar to the rest of the solution species, the negative ions tend to leave the Stern layer with the increased solvation energy, $\epsilon_{\text{s-neg}}$. The presence of negative ions in the Stern layer increases the overall negative charge and attracts positive counterions (both PDIs and non-PDIs). Therefore, as the number of negative ions decreases with the solvation, so does the number of PDIs and non-PDIs as indicated in the figure. The positive ions are being replaced by solvent molecules.

3.1.3 Charge and potential distribution

Solvent-solvent interactions

The charge density distribution, for different values of the solvent-solvent LJ interaction parameter $\epsilon_{\text{s-s}}$, is shown in Fig. 4.4a. The plot exhibits well defined oscillations near the wall, which are due to excluded volume effects as well as longer-ranged correlation between the solution species and excluded volume effects with the interface. The curves are very different from the charge density distributions that correspond to the Boltzmann distribution (3.2), which describes a monotonic function. For low LJ attractions between the solvent molecules (starting with $\epsilon_{\text{s-s}} = 0$), the first peak in the charge density distribution is much lower than the rest. This means that the charge density in the Stern layer is lower. This is due to excluded volume competition from the large number of solvent molecules. These molecules displace ions from the Stern layer and thus deplete it of charges. As the solvent attractive energy (i.e., $\epsilon_{\text{s-s}}$) increases, the solvent molecules are less driven to accumulate near the surface, or interact with the ions. Hence, the height of the first peak increases allowing for (predominantly positive) ions to accumulate in the Stern layer. This in turn leads to less charge in the region right next to the Stern layer (the second set of peaks in Fig. 4.4a). The rest of the peaks decrease in height both with the distance from the surface and with $\epsilon_{\text{s-s}}$. At about $\epsilon_{\text{s-s}} = 0.8$, the first and second peaks have similar
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height and the trend reverses. Above $\epsilon_{s-s} = 0.8$, the first peaks are the highest, indicating that the Stern layer has the greatest bulk charge density compared to the next layers of the solution.

The resultant potential distribution, however, is monotonic, see Fig. 4.4b. Each curve corresponds to a different value of the solvent-solvent interaction parameter $\epsilon_{s-s}$. The potential is most negative in complete absence of any LJ attractions ($\epsilon_{s-s}/k_B T = 0$). As the parameter $\epsilon_{s-s}$ increases (in steps of $0.1k_B T$), the magnitude of the potential decreases. The top curve corresponds to $\epsilon_{s-s}/k_B T = 1.2$. These results demonstrate that even non-Coulombic interactions between neutral molecules have a strong effect on the electrostatics of charged interfaces. All components in a solution are involved in interactions with each other as dictated by thermodynamics, therefore changing the attraction between the solvent molecules inevitably affects their interactions with the ionic species. Among the ionic species are the PDIs, and perturbing their density in the Stern layer (see above) shifts the surface equilibrium (1.19), the interfacial charge and consequently, the bulk charge and potential distributions.

The spatial potential distributions are reasonably well described by exponential curves. While the potential magnitudes exceed the Debye and Huckel regime, they are still moderate, which contributes to such behavior. The Debye screening length for the computations is determined by the total ionic strength (0.01 M) and is given by $\kappa^{-1} = 10.56d$.

Interestingly, the surface potential $\Psi_s$ becomes less negative in a linear proportion to the bulk solvent LJ interactions, or the parameter $\epsilon_{s-s}$ (see the inset in Fig. 4.4b).
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Figure 3.3. Charge and potential in an EDL for variable solvent-solvent LJ interactions $\epsilon_{s-s}$. (a) Bulk charge density distribution at different values for the solvent LJ interaction parameter. Inset: surface charge. (b) Electrostatic potential distributions. Inset: surface potential.

Solvation of the potential determining ions

The PDIs solvation effect on the charge and potential distributions in EDLs is illustrated in Fig. 4.6. Since, the PDIs determine the surface charge, their solvation should have a significant effect on the surface charge and the overall properties of
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the EDL. The solvation interactions of the PDIs compete with the electrostatic interactions with the interface, and with the chemical reaction (1.19).

The spatial charge density distributions are depicted in Fig. 4.6a. In this case the domain with greatest charge density is the Stern layer, which is demonstrated by the highest first peaks. The heights of these peaks however, exhibit a minimum as $\epsilon_{s,PDI}$ varies from 0 to $1.2 \ k_B T$. This behavior is related to the solvation of the PDIs. At low values of $\epsilon_{s,PDI}$, the PDIs interact very weakly (or not at all) with the solvent and hence, they accumulate in the Stern layer. For example, for $\epsilon_{s,PDI} = 0$, the density of PDIs in the Stern layer is $\rho_{PDI} \sim 6.1 \times 10^{-4}$. The positive non-PDIs in the Stern layer have a density $\rho_{Pos} \sim 3.1 \times 10^{-4}$. Note that the PDIs have a 100 times lower density in the bulk compared to the non-PDIs. However, the latter ions are solvated, while the PDIs are not. These are the factors that lead to the particular density values. For $\epsilon_{s,PDI} = 1.2 k_B T$, the respective density values for the two positive ionic species are $\rho_{PDI} \sim 3.4 \times 10^{-6}$ and $\rho_{Pos} \sim 9.7 \times 10^{-4}$. Hence, as the solvation of the PDIs increases, they are removed from the Stern layer into the bulk, which decreases the total amount of positive charge. This however, leads to an increase of the negative surface charge, which in turn attracts positive counterions. Hence the number of positive non-PDIs, which also are in much greater number in the solution, populate the Stern layer thus making it again more positive.

The potential distributions are shown in Fig. 4.6b. In this the stronger the PDIs solvation the more negative is the surface charge. For very weak solvent-PDI attraction $\epsilon_{s,PDI} \simeq 0.2 k_B T$ and below the PDIs are present in large numbers in the Stern layer and turn the surface positive according to (1.19). The shape of the potential distribution curves is still very close to exponential. The surface potential, however, is not a linear function of the solvation energy parameter, in this case $\epsilon_{s,PDI}$. The surface potential $\Psi_s$ becomes more negative with the solvation of the PDIs, because they are effectively removed from the surface into the bulk and the
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Figure 3.4. Charge and potential in an EDL for variable solvent-PDI interactions \( \epsilon_{s-PDI} \). (a) Bulk charge density distributions at different solvent-PDI LJ parameter values. Inset: surface charge. (b) Electrostatic potential. Inset: surface potential.

reaction equilibrium (1.19) is shifted in direction of greater dissociation.
Solvation of the positive non-potential determining ions

The effect of the positive non-PDIs solvation is illustrated in Fig. 3.5. The charge density distribution curves at different values of $\epsilon_{s-\text{Pos}}$ (Fig. 3.5a) exhibit noticeable peaks that correspond to the accumulated positive charge in the Stern layer. These peaks
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peaks are much higher than those further away from the surface, which while present are hard to detect at this scale. The Stern peaks, corresponding to various positive ions solvation, are also more pronounced than the peaks that correspond to the solvent-solvent and solvent-PDI interaction cases discussed above. This indicates that the positive non-PDI tend to accumulate in great numbers in the Stern layer, particularly when not strongly solvated. The peak height rapidly drops as the LJ interaction $\epsilon_{s-\text{Pos}}$ increases. The bulk concentration of the positive non-PDIs is also high (0.01 M) relative to that of the PDIs ($10^{-4}$ M). This certainly facilitates the population of the Stern layer with positive ions, which while not involved in any surface chemical reaction are still subject to Coulombic interactions (with the rest of the ions and the charged interface), and solvation forces (with the solvent molecules.)

The potential distribution in the EDL is displayed in Fig. 3.5b. Low solvation of the positive ions leads to their accumulation near the interface. As we have established earlier, [64] the large number of positive ions in the Stern layer create an exclusion volume and electrostatic barrier for the PDIs to reach and chemically react with the surface. Hence, the interface tends to be more negatively charged. Note that despite the positive surface potential for low solvation interactions ($\epsilon_{s-\text{Pos}} \lesssim 0.2 k_B T$) the surface charge is still very negative, since $\sigma = -\varepsilon \varepsilon_0 (\nabla \Psi)_s$. The steep change in the potential very near the charged interface corresponds to the capacitance effect of the Stern layer. [86] The potential distribution beyond the Stern layer is very close to exponential. The surface potential changes from weakly positive to moderately negative as $\epsilon_{s-\text{Pos}}$ varies from 0 to 1.2 $k_B T$, and shows a trend to leveling off at large values of the LJ interactions.

Solvation of the negative non-potential determining ions

Fig. 3.6 shows the effect of negative ion solvation on the charge and potential distribution in an EDL. The charge distribution is depicted in Fig. 3.6a, and it shows
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Figure 3.6. Charge and potential in an EDL for variable solvent-negative ion interactions $\epsilon_{s-Neg}$. (a) Bulk charge density distributions at different solvent-negative ions LJ parameter values. Inset: surface charge. (b) Electrostatic potential. Inset: surface potential.

a very different behavior compared to all cases discussed above. The reason is that the negative ions has a sign opposite to the PDIs and the rest of the positive ions. Hence, when poorly solvated (or not at all) they tend to accumulate near the surface forming a Stern layer with predominantly negative charge. This is most pronounced for $\epsilon_{s-Neg} = 0$ and increases with the LJ attraction between the negative ions and the
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solvent molecules. This negative charge is effectively added to that of the surface. At about $\epsilon_{s-Neg} \gtrsim 0.7k_B T$ the charge in the Stern layer changes from negative to positive, which is due to removal of negative ions into the bulk with the increased solvation.

The potential distribution curves become less negative as the LJ parameter $\epsilon_{s-Neg}$ characterizing the solvation interactions increases. The effect levels off at greater solvation interactions. This trend is also seen the in plot for the surface potential.

3.2 Conclusions

The electric double layer is a central concept in research fields such as fundamental electrochemistry, colloid science, biophysics, material science, corrosion and many others. The approach outlined in this study can be directly applied to problems in these areas. For example the replacement of A with AlO$^-\text{and B with OH}^-\text{in Eq. (1.19), represents a corroding aluminum interface in contact with water.}$

The properties of electric double layers are determined by the electrolyte solution thermodynamics in the presence of a charged and chemically reactive interface. This implies that all components play a role, including those that are not charged and therefore, insusceptible to Coulombic type of interactions. An example for such a component is the solvent. Typically, the solvent is present in amounts that strongly exceed those of the dissolved ionic species. The solvent molecules interact among themselves and with the rest of the components through non-Coulombic interactions, due to van der Waals molecular forces. These are known as solvation interactions and, despite their non-electrostatic origin, have a strong impact on the properties of electric double layers. The solvation interactions essentially compete with the interactions with the charged interface. Hence, they affect the distribution of solutes in the system, including in the Stern layer. A particularly important component of
the Stern layer is the potential determining ion. These ions chemically interact with
the surface ionizable groups and therefore, their local concentration is directly related
to the dissociation-association equilibrium that determines the actual surface charge.
Obviously, the surface charge is an important factor that sets the distribution of all
charged species in the solution.

The solvent-solvent interactions do no directly involve and charged species and
yet, their effect is significant. The solvent molecules occupy a considerable fraction
of the Stern layer and hence, determine its overall charge. A linear relationship
between the surface potential and the energy parameter for the Lennard-Jones solvent
attraction is observed.

The solvation of the potential determining ions also affect the properties of the
electric double layers. The main factor that plays a role in this case is the surface
reaction. In the presence of additional and chemically inert ionic species, the charge
density in the Stern layer exhibits a minimum with the variation of the potential
determining ions solvation strength.

The positive non-potential determining ions interaction with the solvent also has
an effect on the properties of the electric double layer. Depending on the strength of
the solvation interactions, these ions accumulate in different quantities in the Stern
layer and thus, determine its charge. The positive ions, while chemically inert with
respect to the surface, may serve as an excluded volume/electrostatic barrier for
the potential determining ions and hinder their access to the interface. Hence, the
positive ion solvation can indirectly affect the surface charge.

The solvation of the negative ions may have a dramatic effect on the electric
double layer. When poorly solvated these ions accumulate the Stern layer and add
more negative charge to an already negative surface. A strong solvation of the
negative ions, however, eliminates this effect.
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Charged interfaces involving electrolytes are complex systems. Their properties depend on many factors, some of which are unrelated to electrostatic interactions. This observation is in accord with the great number of experimental data showing that the properties of electric double layers may differ when different types of ions having the same charge are involved.
Chapter 4

Surface -solution interactions in charge regulating double layers

4.1 Introduction

These interactions generally involve charged solutes that attach to the surface or alternatively, surface groups may dissociate releasing a ions into the solution. EDLs are a complex multicomponent systems, where all participating species interact with each other. The charge interface is one such component, and the same is true for neutral solvent. The surface and the dissolved ionic species might be involved in a number of complex chemical interactions. The solvent is also involved in solvation interactions both with the ions and the substrate. The solvation forces interfere with the direct ion-surface interactions and also play an important role on the local density distributions of all solution components.

We demonstrated that the detailed molecular structure of electrolyte solution near a charged interface couples to the specific surface chemistry that governs the charge. A major factor that determines the solutions structure are the
molecular interactions and correlations with the solvent. This implies that the solvent has an extremely role for the properties of the EDL, despite the fact that it is usually neutral and therefore, not involved in any electrostatic interactions.

This chapter investigates in detail the effect of all non-Coulombic interactions between the solution species and the surface. We examine the contribution of solvophilicity and solvophobicity, as well as possible ion-surface attractions that may lead to physical adsorption. These interactions would have an effect on the over properties of EDLs including the composition of the very important first layer next to the surface, known as the Stern layer. Following the historical tradition, we refer to the location of the interfacial charge as the inner Helmholtz plane (IHP), while the Stern layer is placed at the outer Helmholtz plane (OHP). Our analysis is based on the classical density functional theory (cDFT).

4.2 Results and Discussion

4.2.1 Effects of the Non-Electrostatic Solution-Surface Interactions on surface charge and charge of stern plane

All solution species experience various interactions with the surface. It is obvious that the ions exhibit electrostatic interactions with the charged interface. However, the focus in this subsection is on non-electrostatic forces of LJ type [see (1.16)]. These interactions in combination with the solvation (see the previous subsection) determine all effects that are unrelated to charges but known to exist and affect the surface charge and the overall properties of EDLs.
Chapter 4. Surface-solution interactions in charge regulating double layers

Figure 4.1. Effect of LJ interactions with the wall for PDIs (solid curves), non-PDI positive ions (dashed curves), solvent (dot-dashed lines) and negative ions (dotted curves) on the surface charge. All other parameters are as in Fig. 2.1a. Panels (a) and (b) show the charge at the IHP. Panels (c) and (d) depict the charge at the SP. Panels (b) and (d) provide more detailed resolution of complex dependence of the surface charge on the LJ interactions for lower values of $\epsilon_i/k_B T$.

Fig. 4.1 presents DFT results for the surface charge vs the LJ interaction energy with the interface for each component. The surface is characterized by pI = 2, $\Delta pK = 8$ and it is in contact with solution that has pH = 4. The data in Figs. 4.1a and 4.1b shows the charge at the IHP, while Figs. 4.1c and 4.1d refer to the charge at the SP after the Stern layer. Figs. 4.1a and 4.1c cover a wider range of species-wall interaction energies. Figs. 4.1b and 4.1d show the details at moderate surface attraction, which are rather complex.

Both the IHP and SP charge values suggest that the effect of the surface interaction for the PDIs and the solvent are similar. As the PDIs get more attracted...
to the surface, their local concentration increases and the equilibrium (1.19) shifts towards lower number of the negative $A^-$, and higher number of neutral $AH$, or even positive $A^+_2$ surface groups. This effectively shifts the charge at the IHP and shear plane to less negative values. One important difference is observed for large values of $\epsilon_{\text{PDI}}/k_B T$. The rate of change of the charge at the IHP tends to decrease, while it is almost constant at the SP. The reason is that the charge at the IHP depends on the chemical equilibrium (1.18), which determines how many of the surface groups turn from negative to neutral or positive. The charge at the SP however, is governed not only by the surface reaction, but also on the accumulation of positive PDIs in the Stern layer. The charge of these ions adds to the charge at the IHP, which leads to much stronger positive shift.

In contrast, the effects of the positive non-PDIs on the charges at the IHP and SP are very different. As the LJ attraction of the non-PDIs to the surface increases, the charge at the IHP starts decreasing and above $\epsilon_{\text{non-PDI}}/k_B T \simeq 5$ sharply drops down to $\sigma d^2/e = 0.664$, which corresponds to complete dissociation of all surface groups [see Fig. 4.1a and Eq. (1.18)]. The reason for this strong effect follows from the fact as non-PDIs accumulate in great numbers near the charged surface, they create a excluded volume and electrostatic barrier for the PDIs to approach the surface and participate in the surface chemical reactions. Hence, the charge at the IHP increases to its maximum value. On the other hand the charge at the SP responds very differently to the increased attraction of the non-PDIs to surface (see Fig. 4.1b). In this case the surface charge becomes more positive, because of the accumulation of positive ions in the Stern layer. The observable charge at the SP is a difference between the negative surface charge at the IHP minus the positive ions in the Stern layer. Hence, as more positive ions populate the Stern layer, the more positive the SP charge becomes.

The LJ interaction of solvent molecules with the charged surface also has a
strong effect both on the charge at the IHP and SP. This interaction determines
the solvophilic/solvophobic properties of the material in contact with the electrolyte
solution. As the surface becomes more solvophilic, the surface charge becomes more
negative and above $\epsilon_s/k_BT \simeq 24$ reaches the fully dissociated state, where again
$\sigma d^2/e = \pm 0.664$. This effect is entirely due to displacement of PDIs (as well as other
ions) through simple excluded volume interactions. The dependencies on both Figs.
4.1a and 4.1b look very similar. The reason for that is because the Stern layer is
exclusively populated by uncharged solvent molecules and therefore there is practi-
cally no charge screening between the IHP and the SP. The charge on both sides of
the Stern layer (see Fig. 1.1) is almost identical.

The effect of the negative ions present in the solution on the charge at the IHP is
negligible (see Fig. 4.1a), and is significant on the charge at the SP (see Fig. 4.1c).
The charge at the IHP is determined by the surface chemistry and the negative
ions do not affect it much (see Fig. 4.1a). On one hand they are attracted to the
surface and occupy volume, which should prevent PDIs from approaching the surface
and participating in the equilibrium (1.18). The excluded volume effect however is
offset by the electrostatic attraction that all positive ions experience and the overall
effect is insignificant. The charge at the SP, however, becomes more negative as
greater numbers of negative ions are attracted to the surface. The dependence on
the attractive LJ energy becomes more pronounced with $\epsilon_{\text{negative ion}}/k_BT$ and for
large values linearly decreases. It may be expected that at even higher energies the
charge dependence may level off when the whole Stern layer is entirely populated by
negative ions, add negative charge to the one already at the IHP.
Figure 4.2. Mole fraction of solution components as a function of the solvation interaction of various species. The different lines correspond to PDIs (solid line), positive non-PDIs (dashed line), negative ions (dotted line), and solvent (dot-dashed line). (a) Varying solvent-wall LJ interactions; (b) Varying PDI-wall LJ interactions; (c) Varying positive-wall LJ interactions; (d) Varying negative-wall LJ interactions.

4.2.2 Composition of the Stern layer

The mole fraction of a component is calculated from the density profiles. If $\rho_i^{st}$ is the density of a component in the stern layer, $L$ is the thickness of Stern layer, which is taken after the first minimum of density profiles

$$\rho_i^{st} = \int_0^L dz \rho_i(z)/L.$$ (4.1)
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The mole fraction $x_i$ of component $i$ is given by

$$x_i = \frac{\rho_{st}^i}{\sum_{i=1}^{M} \rho_{st}^i}. \quad (4.2)$$

The composition of the Stern layer is of crucial importance for the properties of the charged interface. It determines the local density of PDIs, and hence the surface charge [see (1.19)]. It is also related to the shear plane, which is a key concept in electrokinetic phenomena. [59–63]

The composition of the Stern layer is determined by the interaction of each component with the wall (both Coulombic and non-electrostatic) relative to the interactions in the fluid. In this section we examine the wall LJ interactions of various components, while keeping all fluid LJ interactions equal to $1k_B T$.

Fig. 4.2 presents the results for the mole fraction composition of the Stern layer as the wall interactions for each of the four fluid components is varied one at a time, while the rest are set to $1k_B T$.

Fig. 4.2a shows the results for varying the solvent-wall LJ attraction. The number of solvent molecules vastly exceeds the numbers of all other components. For solvent molarity 55.6 M and ionic strength 0.01 M, we have about 5,500 solvent molecules per ion. The ratio is even more extreme for the PDIs. At pH = 4, there are 550,000 solvent molecules per PDI. Hence, it is not surprising that the solvent molecules tend to dominate the Stern layer, even at very low values of $\epsilon_{S-W}$, where the background electrolyte ions and the PDIs also get into the Stern layer due to the LJ attraction with the wall that they are experiencing. Of all ionic species, the positive non-PDIs populate the Stern layer in greatest numbers because they are also attracted to the negative wall by means of electrostatic interactions [see Eq. (1.17)]. The negative ions are attracted by LJ forces to the wall, but they are electrostatically repelled, hence their density is lower. The PDIs are attracted by both LJ and Coulombic
interactions into the Stern layer. However, their overall number is substantially lower than all the rest of the solution components. In addition part of the PDIs get consumed by the reaction (1.19). As a result, their number in the Stern layer is the lowest.

The effect of the LJ attraction of the PDIs to the charged wall is shown in Fig. 4.2b. The PDIs are a subject of complex and diverse set of surface interactions that include electrostatic (see Eq. (1.17)), LJ (see Eq. (1.16)), and chemical (see Eq. (1.19)). The latter governs the overall charge of the EDL.

If the PDI-wall LJ attraction is low (i.e., $\epsilon_{\text{PDI-w}} \lesssim 5$), then the region next to the charged surface is mostly populated by solvent molecules. As the parameter $\epsilon_{\text{PDI-w}}$ increases, the mole fraction of PDIs in the Stern layer also increases. This leads to a significant reduction of the negative surface charge (see Section B), which in turn facilitates the increases of the mole fraction for the negative ions in the Stern layer. Above certain value of the LJ attraction energy parameter ($\epsilon_{\text{PDI-w}} \gtrsim 3.15k_B T$), the surface charge turns positive. The PDIs continue to accumulate in the Stern layer, but at lower rate because of the electrostatic repulsion from the positive surface. The negative ions mole fraction passes over a maximum, and starts decreasing for $\epsilon_{\text{PDI-w}} \gtrsim 12k_B T$ because their are displaced by the PDIs through excluded volume interactions. The positive non-PDIs are practically absent from the Stern layer.

Fig. 4.2c: shows the effect of the LJ attraction of the positive non-PDIs to the charged wall. The positive ions are also attracted by the surface charge, which is negative in this case. The PDIs and the negative ions are in relatively small amounts. Hence, the main competition for space in the Stern layer is between the positive ions and the solvent molecules. As the mole fraction of positive ions increases (with $\epsilon_{\text{Pos-w}}$), they create an electrostatic and excluded volume barrier for the PDIs, which are then further excluded. This leads to an increase of the surface charge [see Eq. (1.19)], and that attracts even more positive ions into the Stern layer. About
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$\epsilon_{\text{Pos-w}} \gtrsim 15$, the Stern layer is almost entirely occupied by positive non-PDIs. This has a profound effect on the charge and potential distribution in the nearby fluid (see Section B).

Finally we consider the effects of negative ions LJ attraction to the wall on the composition of the Stern layer (see Fig. 4.2d). At low attraction ($\epsilon_{\text{Neg-w}} \lesssim 4$), the Stern layer is primarily occupied by solvent. At higher values, the negative ions mole fraction in the Stern layer begins to increase and it is almost immediately followed by an increase of the amount of positive ions. This applies to both PDIs and non-PDIs, although the mole fraction of the former is barely noticeable at this scale. Still, the PDIs neutralize the surface negative charge [by means of Eq. (1.19)] even turn it positive (see Section B). The greater positive surface charge in combination with the excluded volume competition from the negative ions ultimately leads to a decreasing trend for the mole fraction of positive ions in the Stern layer after passing over a maximum at $\epsilon_{\text{Neg-w}} \approx 12$.

4.2.3 Charge and potential distribution

Solvent-surface interactions

A surface, in contact with solution, can be characterized as solvophilic or solvophobic depending in its interactions with the solvent molecules. We account for this interaction via Eq. (1.16). In the analysis below, a surface is considered solvophobic if the LJ parameter for the solvent-wall interaction $\epsilon_{\text{S-w}}$ is less that the LJ interactions between the solution species in the fluid $\epsilon_{ij}$. It is solvophilic if the solvent-wall interaction $\epsilon_{\text{S-w}}$ is greater that $\epsilon_{ij}$.

Solvophobic surfaces and the solvophobic-solvophilic transition. It is of fundamental interest to study how the properties of EDLs would change as the
interface gradually changes from solvophobic to solvophilic. These properties include the charge density and potential distributions (see Fig. 4.3). The charge density
distribution [Eq. (1.22)] is shown in Fig. 4.3a. The first set of peaks on the left in the figure correspond to the Stern layer. The charge density in this layer is higher for a solvophobic surface i.e., $\epsilon_{s-w} < k_B T$, and decreases as the surface becomes more hydrophilic. In parallel to that, the second (and higher order) set of peaks is barely detectable for low $\epsilon_{s-w}$ but they rapidly increase with the solvophilicity. This complex behavior is due to the interplay between ionic accumulation in the Stern layer and the surface chemical reaction (1.19). The Stern layer at a solvophobic surface is predominantly populated by ions, which are attracted into it by the LJ interactions, equal to $k_B T$ for all species (except the solvent). If the PDIs are not attracted stronger than the rest of the ions, the surface is negative. Hence, positive ions will dominated the Stern layer as indicated by the figure. The positive ions include the PDIs, which reduce the surface charge, by shifting the equilibrium (1.19) towards a more neutral surface (see the inset in Fig. 4.3a). As the surface turns more solvophilic, the solvent molecules begin displacing ions from the layer adjacent to the IHP and the charge density there decreases. However, since the PDI number in the Stern layer drops, the equilibrium (1.19) shifts towards more negative surface charge (see inset). This attracts positive counterions, which accumulate in the second layer. The crossover region, where the heights of the first and second peaks are approximately the same is at $\epsilon_{s-w} = 1.5k_B T$. As a results the Stern layer (or the OHP) is shifted by about one molecular diameter further away into the fluid.

The potential distribution also strongly depends on the surface solvophilicity-solvophobicity properties (see Fig. 4.3b). The potential distributions show negative values that drop with the distance from the surface. The potential magnitude is low for solvophobic surfaces and becomes more negative as the surface turns more hydrophilic. The same is true for the surface potential (see inset), which follows a very similar behavior as the surface charge.
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**Strongly solvophilic surfaces.** Strongly solvophilic surfaces are almost entirely coated with solvent molecules and the number of ions in the first layer is very much reduced. Fig. 4.4a depicts the charge density distribution and it is practically zero at $z/d = 1$. However the charge densities in the second layer are significant and much greater in magnitude than those for solvophobic, or surfaces around the solvophobic-solvophilic transition region (see Fig. 4.3a). The surface charge (see inset) becomes more negative with the solvophilicity and levels of at $\sigma d^2/e = -0.66$ where all surface groups are fully dissociated.

The shift of the charge density away from the substrate-solution interface means that effectively the location of Stern layer moves further into the solution bulk. The closest layer to the surface is practically devoid of charges.

The potential distribution (Fig. 4.3b) becomes more negative with $\epsilon_{s-w}$. The surface potential (see inset) follows the surface charge curve, However, while the surface charge levels off $\sigma d^2/e = -0.66$, the potential continues its change towards more negative values. The values of the potential for very solvophilic surfaces seems to exceed the values for typical materials in aqueous electrolytes. [38] Still it is instructive to look at the extreme case where the surface is fully dissociated and noticing that, unlike the charge, the potential continues to become more negative with $\epsilon_{s-w}$ albeit at lower rate.

Potential determining ions – wall interactions

**Weak and moderate adsorption of potential determining ions.** The potential determining ions also may interact with the charged substrate by means of LJ forces [see Eq. (1.17)]. This interaction affects their overall concentration in the vicinity of the interface (the Stern layer) and hence, the surface equilibrium (1.19) (see Fig. 4.5a). For low LJ attraction (i.e., $\epsilon_{PDI-W}$) the PDI concentration in the
Stern layer is low, which leads to more negatively charged surface (see also the inset). This negative surface charge attracts positive non-PDIs into the Stern layer, which leads to the well-pronounced peaks around $z/d = 1$. As the PDIs become more attracted to the surface with the increase of $\epsilon_{\text{PDI-w}}$, the gradually neutralize the
surface and the numbers of non-PDIs drop accordingly, thus reducing the positive charge density in the Stern layer. Further increase of $\epsilon_{\text{PDI-w}}$ saturates the Stern

![Figure 4.5](image)

Figure 4.5. Charge and potential in an EDL for variable PDI-wall LJ interactions $\epsilon_{\text{PDI-w}}$. Weak to moderate interactions case. (a) Bulk charge density distribution at different values for the solvent LJ interaction parameter. Inset: surface charge. (b) Electrostatic potential distributions. Inset: surface potential.
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layer with PDIs, which again increases the total positive charge density there. The surface charge becomes less negative and, at $\epsilon_{\text{PDI-w}} \sim 3.15k_BT$, turns positive.

The potential distributions at different values of $\epsilon_{\text{PDI-w}}$ are shown in Fig. 4.5b. The potential magnitudes both in the fluid and at the surface decrease with the PDI-wall attraction. The sign of the potential also changes as $\epsilon_{\text{PDI-w}}$ exceeds 3.15 $k_BT$. The surface potential follows the same qualitative trend (see inset).

**Strong adsorption of potential determining ions.** Strong physical adsorption of PDIs to the surface increases their concentration in the Stern layer and turns the surface charge and potential even more positive [see Eq. (1.19) and Fig. 4.6]. This leads to the attraction of negative ions in the Stern layer (see the negative dip on the left of the peaks in Fig. 4.6a). The dip minimum is shifted closer to the wall and away from the positive maximum at a distance about $z/d \sim 0.1$. Hence, the increase of PDIs concentration in the Stern layer due to LJ attraction is accompanied by an increase also of the number of negative ions (see also Fig. 4.2b). The number of PDIs still dominates, which leads to a layer of negative ions on the right of the positive Stern layer peak where another negative charge dip is formed. Hence, the increased attraction of PDIs to the surface leads to a pronounced layering of negative and positive charges next to the interface. However, the positive and negative charges are cannot be placed on the same OHP.

The potential distributions are plotted in Fig. 4.6b. The potentials are positive and for very strong LJ attraction $\epsilon_{\text{PDI-w}}$ may be extremely (perhaps unphysically) positive. The linear portion in the curves at low $z/d$ corresponds to the potential drop between the positive charged surface and the negative charges in the Stern layer (i.e., the Stern capacitor). The positive surface potential (see inset) approaches a linearly increasing asymptote for high PDI adsorption.
Figure 4.6. Charge and potential in an EDL for variable PDI-wall LJ interactions $\epsilon_{\text{PDI-w}}$. Strong surface attraction case. (a) Bulk charge density distribution at different values for the solvent LJ interaction parameter. Inset: surface charge. (b) Electrostatic potential distributions. Inset: surface potential.

Positive non-potential determining ions – wall interactions

Weak and moderate adsorption of positive ions. The presence of positive ions in the Stern layer, near the charged interface is important because they compete with
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the PDIs, which have the same charge (see Fig. 4.7). At low LJ attraction ($\epsilon_{\text{Pos-w}} < k_B T$) the positive ions are absent or in very low amounts in the Stern layer as seen in Fig. 4.7a. This enable the PDIs to accumulate there, since they are attracted, both by means of Coulombic [see Eq. 1.17] and LJ interactions ($\epsilon_{\text{PDI-w}} = k_B T$). Hence, for low $\epsilon_{\text{Pos-w}}$ the Stern layer is populated by PDIs, which neutralize the negative surface charge (see inset). As a result, the overall positive counter-charge in the Stern layer is also low. Increasing the LJ attraction for the positive ions increases their concentration in the Stern layer, thus creating both excluded volume and electrostatic barriers for the PDIs and obstructing their access to the reactive surface. The surface charge becomes more negative, which leads to even greater Coulombic attraction of positive ions in the Stern layer as shown by the growing peaks in charge density distribution.

The potential distributions also become less negative as the LJ interaction $\epsilon_{\text{Pos-w}}$ increases (see Fig. 4.7b). Interestingly, unlike the surface charge, the surface potential changes sign and becomes positive around $\epsilon_{\text{Pos-w}} \sim 3.05k_B T$. The slope of the potentials at the interface remains always positive, which corresponds to the negative surface charge and the presence of a Stern capacitor.

**Strong adsorption of positive non-potential determining ions.** As the positive non-PDIs accumulate in the Stern layer, they prevent the PDIs from participating in the surface equilibrium 1.19, and the surface becomes more negatively charged (see Fig. 4.8). This leads to an even stronger electrostatic attraction of positive ions into the Stern layer, which is demonstrated by the growing peaks next to the surface in Fig. 4.8a. This in turn prompts the formation of a layer of negative ions right next to it (see the minima near $z/d \lesssim 2$). Hence, high adsorption of positive non-PDIs induces a layering of alternatively charged ions. As the LJ attraction energy $\epsilon_{\text{Pos-w}}$ exceeds $10 k_B T$ the surface becomes fully dissociated with a surface charge density $\sigma d^2/e = -0.66$ (see inset).
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Figure 4.7. Charge and potential in an EDL for variable positive non PDI-wall LJ interactions $\epsilon_{\text{Pos-w}}$. Weak to moderate interactions case. (a) Bulk charge density distribution at different values for the solvent LJ interaction parameter. Inset: surface charge. (b) Electrostatic potential distributions. Inset: surface potential.

The potential distributions exhibit a complex behavior with the increase of the LJ attraction $\epsilon_{\text{Pos-w}}$. Due to the charge difference between the charged wall interface
Figure 4.8. Charge and potential in an EDL for variable positive non PDI-wall LJ interactions $\epsilon_{\text{Pos-w}}$. Strong surface attraction case. (a) Bulk charge density distribution at different values for the solvent LJ interaction parameter. Inset: surface charge. (b) Electrostatic potential distributions. Inset: surface potential.
(negative) and the Stern layer (positive) there is a sharp linear change in the potential near the surface, which represents the Stern capacitor. Hence, despite the strongly negative surface charge due to the regulation reaction (1.19), it recharges to positive due to an excess of adsorbed positive ions. The surface potential variations with $\epsilon_{\text{Pos-w}}$ is in qualitative agreement with variation of the surface charge (see inset in Fig. 4.8a). It exhibits a moderate positive increase as $\epsilon_{\text{Pos-w}}$ increases to about $3 \ k_B T$ and the positive non-PDIs start appearing in the Stern layer. The surface charge remains very close to zero. However, the surface charge sharply turns negative above $\epsilon_{\text{Pos-w}} \sim 4k_B T$. The potential responds by also becoming negative. Above $\epsilon_{\text{Pos-w}} \sim 10k_B T$, the charge reaches its maximum value of $\sigma d^2/e = -0.66$ and remains constant after that. The Stern layer however, gets even more populated with positive ions. Since the surface charge cannot change anymore, the system responds by driving the potential to less negative and more positive values.

**Negative non-potential determining ions – wall interactions**

**Weak and moderate adsorption of negative ions.** The selected values for the surface chemistry parameters and pH dictate that the charge at the wall interface with the solution would be mostly negative. Hence, the negative ions experience a repulsive force with the wall [see Eq. (1.17)]. However, strong LJ attraction [see Eq. (1.16)] may overcome the repulsive interaction and allow for the negative ions to adsorb in the Stern layer.

Fig. 4.9 shows the charge and potential distributions in EDLs for the case of weak to moderate adsorption of negative ions. The charge density in the Stern layer (see Fig. 4.9a) changes from positive to negative at about $\epsilon_{\text{Neg-w}} \sim 1.6k_B T$. A careful examination of the figure, however, shows that there is a positive charge density peak slightly the closer to the surface and the deep negative minimum is immediately next to it (on the right). This implies that there are positive ions
in the Stern layer (see Fig. 5.2b). The position of the positive charge peaks are shifted a little closer to the wall in comparison with the negative peaks. Hence, at higher values of the LJ energy parameter, the attraction overcomes the electrostatic repulsion and the negative ions populate the Stern layer in numbers comparable to the positive ones. Increasing attractive energy $\epsilon_{\text{Neg-w}}$ brings even more negative ions and at some point their number dominates the population in the Stern layer. Still, there is always a number of positive counterions that is are adsorbed along with the negative ones, drawn in by the strongly negative potential. This positive ions are placed slightly closer to the interface than the negative ones. The surface charge is also affected because a few of the attracted positive ions are PDIs, which react with the surface thus reducing its negative charge (see inset and (1.19)).

The potential distribution (see Fig. 4.9b) is negative everywhere in the EDL. It becomes even more negative as the negative ions accumulate into the Stern layer with the increasing energy parameter $\epsilon_{\text{Neg-w}}$. The surface potential also becomes more negative (see inset). The slope at very small $z/d$ corresponds to the charge change in the Stern capacitor layer.

**Strong adsorption of negative ions.** The strong LJ attraction of negative ions to the charged wall naturally increases their presence in the Stern layer even further and also turns the potentials more negative as shown in Fig. 4.10. It is interesting to point out however, that the number of positive ions near the charged interface also increases (see Fig. 4.10a). As the local negative charge density increases it electrostatically attracts positive charges into the region. These positive ions mix with the negative, but are slightly out of alignment with respect to the OHP. There are visible peaks on both sides of the deep negative charged minima in Fig. 4.10a. The maxima of the positive peaks are shifted about $z/d \sim 0.1$ to the left and right of the deep negative minimum. This trend continues up to $\epsilon_{\text{Neg-w}} \sim 12kBT$. Above that value for the LJ attraction parameter the excluded volume interaction prevent
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Figure 4.9. Charge and potential in an EDL for variable negative ions-wall LJ interactions $\epsilon_{\text{Neg-w}}$. Weak to moderate interactions case. (a) Bulk charge density distribution at different values for the solvent LJ interaction parameter. Inset: surface charge. (b) Electrostatic potential distributions. Inset: surface potential.

the local density of positive ions from increasing any further (see 4.2). Overall this charge-layering behavior is similar to the one observed at strong PDI-wall interactions described above, but in this case the polarity of the peaks is reversed.

The potential distributions are negative and become even more so as the pa-
Figure 4.10. Charge and potential in an EDL for variable negative ions-wall LJ interactions $\epsilon_{\text{Neg-w}}$. Strong surface attraction case. (a) Bulk charge density distribution at different values for the solvent LJ interaction parameter. Inset: surface charge. (b) Electrostatic potential distributions. Inset: surface potential.

rameter $\epsilon_{\text{Neg-w}}$ increases. The strongly negative potential provides an alternative argument for the observed presence of positive ions very near the surface. The magnitude of the negative surface potential increases linearly for $\epsilon_{\text{Neg-w}} \gtrsim k_B T$. 

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4.3 Conclusions

Electric double layers represent complex multicomponent systems. The interface between the solution and the substrate (wall) is itself one of the most important of these components. It interacts both chemically (through the surface charge regulation reaction) and physically (e.g., through Coulombic and Lennard-Jones forces) with various solutes and the solvent. These interactions are could vary from one specific example to another, thus offering a great number of different cases as numerous experimental data suggest.

It is important to point that the non-electrostatic interactions, like Lennard Jones surface attraction, are no less important than the electrostatic ones. Even neutral species, like the solvent, when attracted to the wall may strongly affect the properties of the whole electric double layer. As the solvent molecules get attracted to the wall they displace the ionic species and may shift the Stern layer further away into the fluid. The solvent-wall attraction also facilitates local liquid structuring, which imprint itself also on the charge density distribution.

The non-Coulombic interactions of the potential determining ions with the surface obviously have an impact on the charged interface properties. Their absence, or presence in the Stern layer governs the surface charge by means of the regulation reaction. In addition they compete with the rest of the ionic species for space in the Stern layer, which also affects the system properties. As the number of potential determining ions in the Stern layer becomes high enough they may change the surface charge polarity by shifting the chemical equilibrium. In our example above, this means that the surface obtains the same positive polarity as the potential determining ions. A somewhat unexpected observation is that as the number of positive potential determining ions increases even further it is accompanied by an increased incorporation on negative counterions in the Stern layer.
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The adsorption of positive, non-potential determining ions creates a barrier for the same charged potential determining ions and prevent them from chemically interacting with the surface. This effectively increases the surface charge. The charge in the Stern layer however, becomes more positive with the adsorption and the potential distributions switch from negative to positive. The surface potential exhibits a complex and non-monotonic behavior.

The Lennard-Jones driven adsorption of negative ions occurs (for the selected set of parameters) at a negative surface. As the number of negative ions in the Stern layer increases so does the number of positive ions, although to a lesser extent. This resembles the potential determining ions case where the adsorption of positive ions at a positive interface always leads increased adsorption of negative ions. Hence, it may be concluded that whenever ions are adsorbed at a surface that has the same charge sign, some counterions are always incorporated into the Stern layer because of the strong electrostatic attraction that acts upon them.

Non-Coulombic interactions with the charged surface in an electric double layer have a significant impact on its properties. A proper account of these interactions is a necessary step towards explaining the wide variations in attributes of charged interfaces that are otherwise identical form purely electrostatic perspective.
Chapter 5

Multivalent electrolyte solutions in Double layer

5.1 Introduction

The spontaneous charging of a material in contact with electrolyte solution leads to a spatial redistribution of ions, which is driven by their Coulombic and non-Coulombic interactions with the interface, as well as among themselves and with the solvent. These systems are often referred to as electric double layers (EDLs) and they have been a subject of extensive theoretical and experimental studies for more than a century [1]. EDLs develop at both equilibrium and non-equilibrium interfaces. They represent an important concept that is relevant to surface and colloid science, soft matter and complex fluids, fundamental and applied electrochemistry and corrosion, materials and many other research areas that involve charged interfaces with electrolyte solutions.

Despite the considerable amount of research on EDLs, there are still certain aspects that are not well understood [50][51]. An example is the contribution of
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non-Coulombic interactions and their interplay with the ion-ion Coulombic forces, and the surface chemical equilibrium, which ultimately governs the charge at the interface. Recently, we have examined the role of the solvent interactions on the charge formation, and potential distribution in EDLs and the results suggest that the effect is significant \[36, 64-66, 88\].

It is not surprising, that the ion valency has a strong impact on the properties of charged interfaces. Modern experimental techniques allow to obtain a detailed picture of the charge effects, on the density distributions near the charged surface in an EDL \[89\]. A notable illustration of the effect of the ionic charge number on the properties of charged colloidal systems is the Schulze-Hardy rule, \[90, 91\], which postulates that the critical coagulation concentration of electrolyte, necessary to precipitate charged colloids varies proportionally to the inverse sixth power of the counterion charge number. The theoretical explanation of this rule was one of the great successes of the Derjaguin-Landau-Verwey-Overbeek theory of colloid stability \[90, 91\]. A proper account of the specific surface chemistry further improves the agreement between theory and experiments \[92\].

Understanding the effect of the ionic valency (i.e., charge number) on the properties of EDLs requires an appropriate theoretical description, or else crucial details may be lost. Early attempts to model EDLs with multivalent ions were naturally based on extensions of the Gouy \[2, 85\] and Chapman \[3\] model \[93, 94\]. However, these models, that had been successful in generating decent descriptions of EDL involving monovalent ions, were found to be lacking in the description of the equivalent problem involving multivalent ions \[95, 97\].

We have suggested a more detailed but still very tractable model of electrolyte solutions to study EDLs. Our approach centers around the inclusion of a simple explicit solvent, thereby deviating considerably from the continuum featureless solvent. In addition, we follow Parsegian and Ninham \[39\], and apply a surface
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chemical boundary condition to replace the mathematically more simple alternatives of constant charge and constant potential. The boundary condition, we use, is known as charge regulation, as the surface charge is regulated by the electrolyte conditions (e.g., temperature, pressure, pH) and structure of the interfacial fluid in the vicinity of the boundary. We have shown that, for monovalent electrolytes, the coupled interplay of interfacial structure and surface chemistry produces considerable richness of electrostatic behavior. The current chapter seeks to now extend our understanding to multivalent electrolytes.

As mentioned, we have built our model around the inclusion of a simple explicit solvent. Specifically, the solvent interacts via a Lennard-Jones pair potential with itself as well as the dissolved ions. Admittedly, this constitutes a simplification, as we suppress the polar nature of the most typical aqueous solvent. Similarly, we do not take account of hydrogen bonding or polarizability. Our choice is motivated by our desire to be able to continue to use classical density functional theory \[15,18,20,67\] as our technique to study EDLs, and to enable a straightforward comparison with our recent work on monovalent electrolytes.

We have demonstrated that cDFT can address explicit solvent structure, and charge regulation that governs the surface charge \[36,64,66,88\]. A strength of cDFT is its computational efficiency in comparison with methods such as molecular dynamics, or Monte Carlo. Hence, it allows for comprehensive parameter sweeps that are not feasible with computer simulations. However, an extensive comparison of molecular density profiles, obtained by cDFT, against MD showed an excellent agreement \[98,99\]. This analysis suggests that cDFT is a viable alternative to computer simulations.

The present chapter presents results on the effects of the non-Coulombic interactions and their coupling to the solution and surface interactions involving multivalent ions. These interactions are responsible for the ionic and surface solvation as well as
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for the specific (non-electrostatic) physical adsorption of ions at the interface \[38\]. Our results demonstrate the impact of non-Coulombic interactions on the surface charge regulation equilibrium, and the overall properties of charged interfaces.

![Diagram of electrolyte solution near a charge-regulating interface.](image)

Figure 5.1. A sketch of electrolyte solution near a charge-regulating interface. The dashed lines depict the reactive surface (left) and the outer bound of the Stern layer (right). $q^+$ and $q^-$ are the charge numbers for the background electrolyte ions. For symmetric electrolytes $q^+ = q^-$, while for asymmetric electrolytes $q^+ \neq q^-$. 

5.2 Results and Discussion

5.2.1 Ion density distributions in the electric double layer and composition of the Stern layer

The ion density distributions in an EDL near the charged surface are shown in Fig. 5.2. Fig. 5.2a shows the density distributions for the positive ions, i.e. the counterions to the negatively charged interface. Since the ionic strength is fixed at $I = 0.01$ M the bulk densities of the ions vary. The total number of ions is the
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greatest for the case of 1:1 electrolyte and is the lowest for the 3:3 case. Despite the low overall density of the ionic species the profiles exhibit well defined peaks, resembling a liquid-like structure. Each curve has been normalized by the density value at infinity. Hence, the peaks show the relative change in density with respect to the one in the bulk. This structure is imposed on the ions by solvent, which is much more numerous.

The curves in Fig. 5.2a assemble in three distinct groups. The top three curves are for a trivalent positive ion. The group in the middle is for a divalent positive ion and one at the bottom is for a monovalent positive ions. Within each group the top curve is for the trivalent negative ion, the middle curve corresponds to the divalent negative ions and the bottom curve – to monovalent negative ions.

The significance of the surface charge is evident by negative slope at larger distances. The peaks near the wall (i.e., the OHP) are highest for salts with trivalent positive counterions (3:3, 3:2, and 3:1). Next are the divalent positive counterions (2:3, 2:2, and 2:1), and finally – the monovalent positive counterions (1:1, 1:2, and 1:3). This is due to Coulombic attraction to the negative wall, which is proportional to the ion charge [see Eq. (1.17)].

The effect of the negative ions on the distribution of the positive ones is more subtle. The small variation between the curves within a group are due to the fact that densities profiles are normalized by their constant values in the bulk solution. As the valency of the negative ions vary from one curve to another (while keeping the positive constant) the ion number density also has to vary in order to maintain a constant ionic strength of 0.01 M. Hence, the solid curves in Fig. 5.2a are at the top within each group, because the negative ions is trivalent, and the overall ion densities in the bulk are the lowest. The dashed curves correspond to divalent negative ions and the ion densities are higher. The dotted curves are for monovalent negative ions and therefore the bulk ion densities are the highest. Hence, when normalizing the
Figure 5.2. Ion density profiles near a charge-regulating interface. All curves show the local changes in the ion-densities relative to their values in the bulk solution. (a) Positive ions. Top curves (black): 3:3 (solid), 3:2 (dashed), 3:1 (dotted); Middle curves (red): 2:3 (solid), 2:2 (dashed), 2:1 (dotted); Bottom curves (blue): 1:3 (solid), 1:2 (dashed), 1:1 (dotted). (b) Negative ions. Top curves (dotted): 3:1 (black), 2:1 (red), 1:1 (blue); Middle curves (dashed): 3:2 (black), 2:2 (red), 1:2 (blue); Bottom curves (solid): 3:3 (black), 2:3 (red), 1:3 (blue).

curves, the solid curves data are scaled by the lowest factor, the dashed curves by a greater factor, and the dotted curves – by the greatest. That is why the solid curves
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appear the highest, the dashed are in the middle and the dotted ones are at the bottom of each group.

Fig. 5.2b presents the density distributions of the negative ions near a negative, charge-regulating surface. As in Fig. 5.2a, the density profiles are normalized by their bulk values. The curves are again assembled in groups of three, this time based on the charge number of the negative ions. The top three curves are for the monovalent negative ions, which experience a weaker repulsion from the negative wall. The middle group of curves corresponds to the divalent negative ions and the lowest three curves are for monovalent negative ions. In this case the ions are repelled from the surface via Coulombic repulsion.

The effect of the positive ions on the density profiles of the negative ions is weaker. The variations within a group of curves is due to the same curve scaling with the bulk densities that was explained above.

The actual mole fractions of the positive and negative non-PDIs in the Stern layer (for all the different cases) are shown in Table 5.1.

Fig. 5.3 depicts the normalized density profiles of the PDIs for different types of background electrolyte, while the Debye screening length is constant, \( \kappa^{-1} = 10.6d \). For \( d = 0.288 \text{ nm} \) this translates to dimensional Debye length of 3.05 nm. The PDI density does not vary with the electrolyte type, since it is determined by the fixed pH = 4. Hence the variations are due to subtle effects exerted by the non-PDI electrolyte type on the potential and charge distributions in the fluid, and at the surface. The mole fraction of PDIs in the Stern layer and for different types of background electrolyte is shown in Table 5.1. The Stern density of PDIs is particularly important because it is responsible for the surface charge regulation through the equilibrium \( (1.19) \).

The mole fraction of each component in the Stern layer is calculated from the
Table 5.1. Mole fractions of solvent and solutes in the Stern layer ($x_i$, $i = s, PDI, Pos, Neg$), surface charge $\sigma d^2/e$, and surface potential $e\Psi_s/k_B T$. The overall ionic strength is adjusted to maintain a fixed Debye length $\kappa^{-1} = 10.6d$. $|q_1|$ and $|q_2|$ are the positive and negative ions charge numbers for the background, non-PDI electrolyte.

| $|q_1| : |q_2|$ | $x_s$ | $x_{PDI}$ | $x_{Pos}$ | $x_{Neg}$ | $\sigma d^2/e$ | $e\Psi_s/k_B T$ |
|----------------|--------|-----------|-----------|-----------|----------------|----------------|
| 1:1            | 0.99955520 | 3.53 $\times 10^{-6}$ | 3.4930 $\times 10^{-4}$ | 9.193 $\times 10^{-5}$ | $-2.150 \times 10^{-3}$ | $-0.7208$ |
| 1:2            | 0.99974090 | 3.67 $\times 10^{-6}$ | 2.4092 $\times 10^{-4}$ | 1.447 $\times 10^{-5}$ | $-2.068 \times 10^{-3}$ | $-0.7581$ |
| 1:3            | 0.99980620 | 3.81 $\times 10^{-6}$ | 1.8677 $\times 10^{-4}$ | 0.317 $\times 10^{-5}$ | $-1.990 \times 10^{-3}$ | $-0.7946$ |
| 2:1            | 0.99972610 | 3.35 $\times 10^{-6}$ | 2.0573 $\times 10^{-4}$ | 6.486 $\times 10^{-5}$ | $-2.263 \times 10^{-3}$ | $-0.6714$ |
| 2:2            | 0.99982120 | 3.42 $\times 10^{-6}$ | 1.6307 $\times 10^{-4}$ | 1.231 $\times 10^{-5}$ | $-2.196 \times 10^{-3}$ | $-0.7002$ |
| 2:3            | 0.99985570 | 3.56 $\times 10^{-6}$ | 1.3760 $\times 10^{-4}$ | 0.314 $\times 10^{-5}$ | $-2.133 \times 10^{-3}$ | $-0.7280$ |
| 3:1            | 0.99977880 | 3.20 $\times 10^{-6}$ | 1.6684 $\times 10^{-4}$ | 5.118 $\times 10^{-5}$ | $-2.369 \times 10^{-3}$ | $-0.6278$ |
| 3:2            | 0.99984320 | 3.27 $\times 10^{-6}$ | 1.4256 $\times 10^{-4}$ | 1.099 $\times 10^{-5}$ | $-2.314 \times 10^{-3}$ | $-0.6503$ |
| 3:3            | 0.99986700 | 3.35 $\times 10^{-6}$ | 1.2652 $\times 10^{-4}$ | 0.314 $\times 10^{-5}$ | $-2.262 \times 10^{-3}$ | $-0.6719$ |

Figure 5.3. Density profile of the PDIs in the presence of different electrolytes. The different curves are (black): 3:3 (solid), 3:2 (dashed), 3:1 (dotted); (red): 2:3 (solid), 2:2 (dashed), 2:1 (dotted); (blue): 1:3 (solid), 1:2 (dashed), 1:1 (dotted).

The density profiles. The density of component $i$, $\rho_{st}^i$, is defined by

$$\rho_{st}^i = L^{-1} \int_0^L dz \rho_i(z),$$  \hspace{1cm} (5.1)
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where $L$ is the thickness of Stern layer determined by the location of the minimum after the first density peak in the profiles. Then the Stern layer mole fraction $x_i$ of component $i$ is

$$x_i = \frac{\rho_{st}^i}{\sum_{i=1}^{M} \rho_{st}^i}.$$  \hspace{1cm} (5.2)

![Graph](image)

Figure 5.4. Total fluid charge density profiles near a charge-regulating interface. The different curves correspond to: (blue): 1:3 (solid), 1:2 (dashed), 1:1 (dotted); (red): 2:3 (solid), 2:2 (dashed), 2:1 (dotted); (black) 3:3 (solid), 3:2 (dashed), 3:1 (dotted).

Table 5.1 presents results for the mole fraction of all solutes in the Stern layer, as well as the resultant surface charge and potential for different types of electrolytes. The data demonstrate that the composition of the Stern layer is dominated by solvent molecules. This may not be always the case if some of the ions exhibit a specific (non-Coulombic) attraction to the substrate (see below). The data in Table 5.1 show that greater charge numbers (i.e., $|q_1|$) of the positive non-PDIs lead to a reduction of their mole fraction in the vicinity of the charged interfaces. This is due to the fact that for a given ionic strength, the necessary number of ions goes down with
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their charge. Ions with greater charge number provide better screening of the surface charge, and hence fewer are needed for keeping the Debye screening length $\kappa^{-1}$ fixed. Even more importantly, the PDIs follow the same pattern. Their mole fraction in the Stern layer decreases with the charge of the positive ions. This in turn leads to higher values for the surface charge magnitude (it becomes more negative) due to a shift in the equilibrium (1.19). The magnitude of the surface potential however, drops with the charge of the positive ions.

The effect of the charge number of the negative ions, $|q_2|$, on the mole fraction of PDIs in the Stern layer is also rather important. The mole fraction of negative ions in the EDL decreases with their charge for the same reason as it does for the positive one. As the negative ion charge increases, less ions are needed to obtain given ionic strength, or equivalently the Debye screening length $\kappa^{-1}$. The effect on the mole fraction of the positive ions is similar – it decreases with the charge of the negative ions. The PDIs however, demonstrate the opposite trend. The mole fraction of the PDIs increases with the charge of the negative ions and that leads to a decreases in the surface charge [see Eq. (1.19)]. The magnitude of the surface potential increases with the charge of the negative ions.

Figs. 5.2 and 5.3 and Table 5.1 imply that the relationship between the electrolyte specific type and the resultant ion distribution, composition of the Stern layer, surface charge and potential is very complex. The ionic charge of the background electrolyte impacts the population of the Stern layer, which then affects the surface chemical equilibrium and therefore the surface charge and potential. The surface charge and potential determine the propagation of the charge and electrostatic potential everywhere in the fluid and these are the physical quantities that specify the spatial distribution of all ionic species. Therefore, there is a chain of interconnected physical effects, all dependent on each other, which governs the observed behavior.
5.2.2 Charge and potential densities

Charge and potential distributions in the fluid

The charge density distribution in the fluid [(see Eq. (1.22))] is plotted in Fig. 5.4 for various types of electrolyte. As the individual charges (valencies) for different ions are varied, the total electrolyte concentration is adjusted so that the Debye screening length remains constant, i.e., $\kappa^{-1} = 10.6d$. The surface is negatively charged (for the selected set of parameter), therefore the valency of the positive counterions has a greater effect on the overall charge distribution. Increasing the charge number of the positive counterions leads to a stronger Coulombic attraction to the negative surface charge and higher peaks in the distribution curves.

The effect of the negative ions is weaker, but still noticeable. Increasing the valency of the negative ions has two effects: (i) it increases the Coulombic repulsion
Figure 5.6. Surface potential and charge at the IHP. The different curves correspond to (black): 3:3 (solid), 3:2 (dashed), 3:1 (dotted); (red): 2:3 (solid), 2:2 (dashed), 2:1 (dotted); (blue): 1:3 (solid), 1:2 (dashed), 1:1 (dotted). (a) surface potential vs adsorption energy for the positive non-PDIs; (b) surface charge vs adsorption energy for the positive non-PDIs; (c)surface potential vs adsorption energy for the negative non-PDIs; (d) surface charge vs adsorption energy for the negative non-PDIs.

with the charged wall interface and (ii) the overall number of ions decreases in order to maintain $\kappa^{-1} = 10.6d$. Hence, the density of negative ions near the negatively charged interface decreases. However, the fixed chemical potential condition requires that some of the positive ions also transfer into the fluid bulk, away from the wall. In addition, the total number of positive ions goes down with the valence of the negative ions, which also leads to a reduction of the net positive charge density in the EDL.
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The potential distributions, corresponding to these charge profiles are shown in Fig. 5.5. Higher valency of the positive ions leads to more negative potentials. The valency of the negative ions however, shows the opposite trend – leading to less negative potentials. The results for the potential distributions, shown in Fig. 5.5 are in agreement with the charge distributions in Fig. 5.4. The magnitudes of the negative surface potentials are highest when the positive ion is monovalent, lower for divalent and lowest for the trivalent positive ions. The effect of the negative ions is the opposite. Higher negative ionic leads to more negative surface potential.

**Adsorption of non-potential determining ions and its effect on the surface potential and charge**

The non-PDIs are not involved in chemical interactions with the surface reactive groups, but still have an indirect effect on the surface charge and potential. They can adsorb at the surface, attracted by non-Coulombic interactions [e.g., see Eq. (1.16)]. The adsorption of ions in the Stern layer alters the local charge and potential, which in turn affect the surface reaction equilibrium and the surface properties.

In addition, some experiments measure the surface potential and charge beyond the Stern layer (such as electro-osmosis or electro-phoresis) will report results that may be very different from the surface potential and charge at the actual physical interface (or the IHP) [38]. Hence, below we present results for the effect ion adsorption on the surface charge and potential at the IHP, as well as at the Stern layer – solution boundary, which is relevant to electrokinetic measurements [59–64].

Fig. 5.6 shows results for the potential and charge at the IHP, which in our model is the reaction interface. The affect of positive non-PDI adsorption on the surface potential is shown in Fig. 5.6a. It exhibits a non-monotonic behavior as the potential initially increases due to the accumulation of positive charges in the
Figure 5.7. Surface potential and charge at the plane beyond Stern layer into the fluid (see the dashed line in Figure 1). The different curves correspond to (black): 3:3 (solid), 3:2 (dashed), 3:1 (dotted); (red): 2:3 (solid), 2:2 (dashed), 2:1 (dotted); (blue): 1:3 (solid), 1:2 (dashed), 1:1 (dotted). (a) surface potential vs adsorption energy for the positive non-PDIs; (b) surface charge vs adsorption energy for the positive non-PDIs; (c)surface potential vs adsorption energy for the negative non-PDIs; (d) surface charge vs adsorption energy for the negative non-PDIs.

immediate vicinity of the negative surface with the adsorption energy $\epsilon_{i-w}$. However, increasing the population of the Stern layer with positive non-PDIs leads to an electrostatic and steric exclusion of the PDIs. This shifts the chemical equilibrium (1.21) towards greater surface dissociation, which leads to more negative surface charge. Eventually the surface dissociation takes over and the potential turns more negative. The position of the observed surface potential maximum depends on the valency of both the positive and negative ions, the positive being more important.
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The maximum occurs first for 1:1 type of electrolyte, followed by 1:2 and 1:3. The surface potential maximum corresponding to the adsorption divalent positive ions is observed at greater adsorption energies. The effect of the negative ions however is similar. The 2:1 electrolyte curve has a maximum at the lowest adsorption energy, followed by 2:2 and 2:3. The curves corresponding to the trivalent positive ions do not show a maximum in the surface chemical potential for the range of adsorption energies we used on our computations, but the there is a clear trend towards one.

The shift of the surface potential maximum, with the valency of both positive and negative ions, is due to the fact that the overall electrolyte concentration is adjusted to maintain $\kappa^{-1} = 10.6d$. Hence, as ion valency increases, the overall number density decreases, and greater attractive energy ($\epsilon_{i-w}$) is needed to fill the Stern layer to the same level. The curves in Fig. 5.6a are bundled in three sets based on the charge number of the adsorbing positive ion. The greater the charge number of the positive ion is the more attraction adsorption energy is needed to compensate for the decreasing ion density effect. Even within a bundle of three curves (where the charge of the positive ions is fixed and the charge of the negative ion varies from one curve to another), there is the same trend present where, the surface potential maximum shifts to greater adsorption energies as the overall ion density decreases.

The effect of the positive non-PDI adsorption on the surface charge at the IHP is shown in Fig. 5.6b. Unlike the surface potential, the surface charge curves exhibit a monotonic trend to acquiring more negative values with the adsorption energy parameter $\epsilon_{i-w}$. Increasing the charge number of either types of ions leads to a decrease of surface charge. The effect is stronger for the adsorbing positive ions.

Fig. 5.7 depicts the effect of ion adsorption on the charge and potential at the outer boundary of the Stern layer (depicted by a dashed line in Fig. 1). While these are not the values at the actual interface between the substrate and the solution, they are more relevant to experimental data like those obtained by electrokinetic
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measurements. The charge and potential at the plane at the outer boundary of the Stern layer could be very different from those at the IHP, which is also evident from the comparison between Figs. 5.6 and 5.7. The overall values are determined by the combination the ionic valency and the number density for given value of the total ionic strength.

The potential outside the adsorption layer which contains predominantly positive non-PDIs is shown in Fig. 5.7a. At lower adsorption energies ($\epsilon_{i-w} \lesssim 3k_B T$) the dominant effect is due to the ion valency. Ions with greater positive charge experience a stronger Coulombic attraction into the Stern layer, in addition to the LJ energy $\epsilon_{i-w}$. They are also more efficient in screening the surface potential and thus, turning it more positive. Hence, the greater the charge of the adsorbed ion, the more positive is the resultant potential. For $\epsilon_{i-w} \gtrsim 3k_B T$ the importance of the positive ion charge, becomes less important, and the ion number density is the governing factor. The greater number of positive ions (i.e., lower ion charge and fixed ionic strength) favors changing the potential from negative to positive, which increases with the ionic density. The effect of the negative ions also seems to be mostly due to the total density. Ions with greater negative charge correspond to lower density of positive and negative ions at fixed ionic strength, which in turn reduced the number of positive ions adsorbed in the Stern layer.

The effect on positive non-PDIs adsorption in the Stern layer on the charge is shown in Fig. 5.7b. As the adsorption energy for the positive ions increases, the charge at the plane immediately after the Stern layer becomes more positive. Again, the ion valency is the dominant factor at low adsorption energies and divalent and trivalent ions can recharge the surface at rather low adsorption energies. This trend is reversed when the ion-wall interaction energy increases, and monovalent ions have a stronger effect on the surface recharging, since they are available in greater numbers to fill the Stern layer.
Fig. 5.7c shows the effect of the negative ion adsorption on the potential after the Stern layer. Both the potential values and the trends, exhibited with the adsorption energy $\epsilon_{i-w}$, are very similar to those for the reactive surface (see Fig. 5.6c). The charge, at outer bound of the Stern layer, is very different from that at the IHP. For low adsorption energies, the Coulombic repulsion prevails and there are few negative ions adsorbed on the Stern layer. This trend is even stronger for multivalent negative ions since their overall number is lower to maintain the fixed ionic strength. This allows the population of the Stern layer with positive ions, which may result in and overall positive charge. As the adsorption energy increases, the number of negative ions in the Stern layer increases and the total charge becomes more negative.

5.3 Conclusions

EDLs are typically characterized by their charge and potential distributions. The charge and potential however, depend on system-specific characteristics such as surface chemistry (i.e., charge regulation), solution pH and ionic strength, and, very importantly, the type of dissolved ions. The ions are involved in Coulombic and non-Coulombic interactions with each other, the solvent and the solution-substrate interface. The local density distributions of the ionic species depends on the charge and potential distribution, but at the same time they affect the surface charge and potential by participating in the charge regulation equilibria (1.19) and (1.19). This complexity implies that the properties of EDLs may vary from one particular case to another, which is in accordance with the experimental observations.

In the present study, we examined the interplay between Coulombic and non-Coulombic interactions by considering ions of different valency. The density distributions of the ions near the charged wall are primarily driven by their Coulombic charge, and the presence of the solvent molecules. The charge of their counterion
partners, also has an effect, albeit smaller.

The combination of Coulombic and non-Coulombic interactions specify the local density distributions of all species including the potential determining ions. The local density of the latter affects the surface chemical equilibrium (i.e., the surface charge and potential). The surface electrostatics in turn determines the density distributions of all charged ions in the solution.
6.1 Introduction

The interaction between charged surfaces, immersed in electrolyte solutions, presents both fundamental and practical interest. Such systems are known as electric double layers (EDLs), and present an essential contribution to the celebrated Derjaguin-Landau-Verwey and Overbeek (DLVO) theory, which offered the first quantitative analysis of the stability of lyophobic colloids. The DLVO theory considers the electrostatic repulsion between colloidal particles as the major stabilizing force that opposes the usually attractive van der Waals interactions. The electrostatic interactions, within the DLVO model, are based on the Poisson-Boltzmann (PB)
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model

$$\nabla^2 \Psi = -\frac{1}{\varepsilon \varepsilon_0} \sum_i \rho_i^0 q_i \exp \left( \frac{-q_i \Psi}{k_B T} \right)$$  \hspace{1cm} (6.1)$$

where $\Psi$ is the local electrostatic potential, $\rho_i^0$ is the number density of solution species $i$ far away from the charged interface, $q_i$ is the charge number of species $i$, $k_B T$ is the thermal energy of the solution, $\varepsilon$ is the relative dielectric permittivity of the solvent, and $\varepsilon = 8.854 \times 10^{12}$ F/m is the dielectric constant of free space.

The PB equation (6.1) assumes that ions are point-like, and do not interact with each other, while the solvent is treated as a structureless continuum. It can be analytically solved for simple (flat) geometries and fixed potential ($\Psi = \Psi_s$) or charge [$\sigma = -\varepsilon \varepsilon_0 (\nabla \Psi)_s$]. [2,3,85,90,91,100]

The continuum treatment of the electrolyte solution, however, fails at short separations between the interacting surfaces that become comparable to the molecular and ionic dimensions. The direct force measurements between surfaces [86,101,102] demonstrated the presence of oscillatory structural forces that are largely due to the excluded volume. The interactions between various species in an electrolyte solution could be rather complex and include short repulsion, Coulombic, van der Waals, dipole-dipole, ion-dipole, etc. Initial theoretical analysis showed that even simple models, that account for the solution molecular structure, are vastly superior to the continuum approach based on the PB equation (6.1). [103–111].

The charging mechanism of the interface is also very important for the overall properties of the EDLs, and hence for the interaction of the surfaces across the electrolyte solution. Fixing the surface potential, or charge provides a convenient mathematical boundary condition, but is not physically justified. The interfacial charge originates from the chemical interactions between certain surface reactive groups and species in the electrolyte solution, a process known as charge regulation. [39,40,43,49]

The surface charge regulation boundary condition is thermodynamically consistent,
and accounts for the material properties of the specific phases that form the EDLs. Recently, we have demonstrated that charge regulation equilibrium strongly depends on the detailed solution structure near the charged interface. [36,64–66,100,112] The surface charge, in turn, affects the local ion density distributions. This coupling between solution structure and surface charge plays an important role for the overall properties of EDLs.

As shown in previous chapters the accurate physical description of surface charge is, that it depends on the chemical equilibrium between the surface dissociative groups with that of potential determining ions in the solution. In this chapter the structural forces and its dependence on electrostatic properties of overlapping double layers are discussed. The effect of non coloumbic interactions like solvation and surface-component interactions also influence the electrostatics of the overlapping double layers.

6.2 Theory

6.2.1 Surface forces and Surface Charge Regulation

The system under consideration is shown in Fig. 6.1. Two perfectly smooth, plane-parallel, and chemically identical surfaces are immersed in electrolyte solution. The distance between the surfaces is much smaller in comparison to their lateral dimensions, therefore edge effect are negligible. The fluid in the gap is in thermodynamic equilibrium with the outside solution, which play the role of a thermal and chemical reservoir. The interactions between the surfaces give rise to an excess disjoining pressure between the surfaces $P_s$, [91] in addition to the hydrostatic pressure for the whole system $P_b$.

We consider a four component solution that consists of solvent, positive potential
determining ions (PDIs) that are involved in chemical interaction with the reactive surface groups, positive but chemically inert ions, and negative counterions. The dimensions of all fluid species are assumed to be the same. The interactions between the solution components include (i) short-range excluded volume (hard core) repulsion, (ii) Coulombic attraction or repulsion (between the ionic species) and (iii) non-Coulombic attraction (e.g., Lenard-Jones), which applies to the ionic species and the neutral solvent molecules. This is known as a semi-primitive model for electrolyte solutions, since it does not take into account any dipole-dipole or ion-dipole interactions that may occur in polar solvent. Despite its approximated nature, the semi-primitive model has been proven to be very helpful in obtaining new insights in detailed structure and the resultant properties of EDLs. The polar solvent effects become important for high electrolyte concentrations and/or in the case of solution-vapor coexistence. Even in that case it was shown that the solvent polarity can be remarkably well accounted for by using a semi-empirical parametrized expression for the dependence of the local dielectric permittivity $\varepsilon$ on the local solvent molecular density $\rho_s(r)$, $\varepsilon[\rho_s(r)]$ instead of explicitly including polar interactions at the molecular scale. Finally, our model is within the mean-field
approximation, and all higher order correlations are ignored. This reasonable for low to moderate electrolyte concentrations. However, for higher concentrations of electrolyte (e.g., 0.1 M and above) the model has to be extended to include the correlation contributions to the thermodynamic functional. [113][114]

The total ionic strength of our model system is 0.01 M hence, using a the semi-primitive approach described above is reasonable. For comparison – the molarity of the neutral solvent is 55.5 M. The molarity of PDIs is $10^{-4}$ M, and the total solution density (scaled with the molecular diameter $d$) is $\rho d^3 = 0.8$.

Forces between charged surfaces in electrolyte solutions.

The interaction energy $\Omega_{\text{int}}(h)$ per unit area $A$ due to the EDL overlap is equal to the total energy [see Eq. (1.3)], at equilibrium is a function of the distance $h$ between the charged surfaces (see Fig. 6.1). It can be written as

$$\frac{\Omega_{\text{int}}(h)}{A} = \frac{\Omega_{\text{eq}}^{\text{edl}}(h)}{A} - \frac{\Omega_{b}^{\text{eq}}}{A},$$

(6.2)

where $\Omega_{b}^{\text{eq}}$ is the bulk fluid energy.

The force per unit area between the surfaces is then

$$\frac{f}{A} = \frac{1}{A} \left( \frac{\partial \Omega_{\text{eq}}^{\text{edl}}(h)}{\partial h} \right)_{\mu,T} = \frac{1}{A} \left( \frac{\partial \Omega_{\text{int}}}{\partial h} \right)_{\mu,T}.$$ 

(6.3)
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Figure 6.2: Density distributions of ionic species and solvent of an electrolytic solution confined between identical charge regulating surfaces with separation distance $h/d_s = 5.0$. The pH=4.0, Ionic strength = 0.01 and $\Delta pK = 8$ a) Potential Determining Ions b) solvent c) Non PDI Positive d) Non-PDI Negative.

6.3 Results and Discussion

6.3.1 Density distributions and properties of confined electrolyte solution

Density distributions

Figure 6.2 shows the equilibrium density distributions ($\rho(r)$) of the different components present in the solution. These density profiles are solutions obtained after minimizing the grand thermodynamic functional ($\Omega(r)$). The separation distance
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Figure 6.3. : Density distributions of ionic species and solvent of an electrolytic solution confined between identical charge regulating surfaces with separation distance $h/d_s = 5.0$. The pH=5.0, Ionic strength = 0.1 and $\Delta pK = 3$ a) Potential Determining Ions b) solvent c) Non PDI Positive d) Non-PDI Negative.

Between the surfaces is $h/d_s = 5.0$. Figure 6.2(a) shows the density distributions of Potential determining ions. The surface dissociation constants are considered $pK^+ = -2.0$, $pK^- = 6.0$ to make the net surface charge negative. PDIs engage in a chemical reaction with the surface dissociating groups to neutralize the surface charge which is given by our charge regulation condition. Since the surface charge is negative, the peaks near the surfaces, which represents the layers of the ionic species with the opposite charge as that of surface, is high. Unlike the continuum models, the intermittent peaks are due to the excluded volume of ionic species and explicit solvent structure that introduces a structural matrix throughout the solution. Figure 6.2(b) shows the neutral species solvent which is not affected the charge on the surfaces but has usual non-columbic structural decay. The figure 6.2(c) is the density distribution
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of Non PDI positive ions which are opposite to the surface charge like PDIs however are not involved in the chemical reaction with the surface. We do not include the size effects in this study. The size of all species is maintained uniform hence the PDI and non PDI Positive densities appear similar but are different in their magnitude which are determined by their bulk density. Figure 6.2(d) corresponds to the density distributions of non-PDI Negative ions. Unlike the PDIs and Positive non-PDIs the first peak is less than the subsequent peaks due to the presence of highly negative charged surfaces on either side of the solution and presence of excessive PDIs and positive non PDIs in the first layer, which creates an electrostatic barrier for negative non-PDI in the stern layer. Hence the negative ions are pushed into bulk.

Electrostatic Potential distributions in confined fluids

Electrolyte solution confined between two identical surfaces consists of the double layers formed by two charged surfaces which overlap for shorter separation distances. This double layer overlap influences the electrostatics of the system. Figure 6.4 shows the electrostatic potential distribution inside the confined electrolyte solution. The electrostatic potential exhibits a monotonic behavior as we have presented a detailed study of electrostatic potentials in the single electric double layers [65, 66, 115]. In this case as the two surfaces with separation distance less than their respective Debye lengths, the electrostatic potential starts decreasing from the surface to that of the mid-plane and starts increasing again due to the presence of the other charge surface. It can be clearly observed that the constant charge or constant potential boundary conditions on the charged surface clearly do not hold good as one surface starts to influence the other. Hence our charge regulation model is appropriate to study the properties of double layers. The charge distribution of the electrolyte solution is minimum as it is at bulk value hence the gradient of the potential is zero at midplane as given by the Poisson equation, which appears as an extremum value (minima or
Figure 6.4. Electrostatic potential distribution normalized with respective surface potentials for various wall separations. Different curves correspond to $h/d_s = 2, 3, 4$ and 5.

maxima depending on the charge of the surface). The farther the separation between the walls, lesser is the influence of external field exerted by the walls on the ionic species closer to the midplane. Hence the minimum in each curve drops for the cases with higher separation distance. Theoretically electrostatic potential can reach closer to zero, if the separation between the walls is infinity, as the charge at the midplane in that case is zero (electro-neutrality).

Another interesting feature captured by this model is that the potential distributions in 6.4 are not smooth. Each curve has their own curvature shifts. To understand these we showed that the total charge density distribution for the corresponding cases of wall separations $h/d_s = 2, 3, 4$ and 5 in 6.5. Poisson equation states that the gradient
of electrostatic potentials are proportional to the bulk charge density distribution in the solution. The figure 6.5, the bulk charge density is quasi layered due to the structure imparted in the solution by solvent, and corresponding to the peaks of charge density in 6.5 the curvature shifts in 6.4 are observed.

6.3.2 Oscillatory structural forces due to the solvent structure

The stability of colloidal suspensions, as given by the Classical DLVO theory, is determined by the competition between attractive van der Waals forces between the surfaces and repulsive double layer forces. However, Classical DLVO theory assumes that the electrolyte consists of point charges in a continuum solvent, so the forces
arise due to varying separation distance between the surfaces show a monotonically decaying behavior mainly due to the decay of electrostatics. However, several experiments and theoretical models already established that classical DLVO fails to account the solvent structural effect at shorter separation distances because DLVO theory is a field theory which is mainly determined by the dielectric constant of the solvent, charge on the surfaces which are bulk properties. Hence this interpretation does not hold good when the separation distances are closer, where the continuum approximation of the solvent is no longer valid. We use Classical Density Functional theory which computes the grand thermodynamic potential of the system which is effective for fluids present in the external fields. So, we treat solvent explicitly.

When the electrolyte solution is confined between the charged surfaces, spon-
Chapter 6. Oscillatory Forces and Surface Charge for confined electrolyte Solutions

taneous redistribution of ionic species occurs across the solution and for shorter separation distances the solution experiences the influence, electrostatic and non-electrostatic, from either surfaces. The neutral species solvent which comprises of higher density when treated explicitly imparts a structural matrix to the solution, because of its excluded volume. This results in forming quasi-layers throughout the solution with certain damping. Hence when the surfaces are approaching each other, these quasi layers of solvent resist the approaching surfaces, which leads to the depletion forces. These are collectively referred as non-DLVO forces as they failed to be captured by classical DLVO theory, as they are dependent on properties like solvation, Surface solution interactions etc. These forces hence are referred to as structural forces or solvation forces, as they arise because of solvent structure.

Figure 6.6 shows the observed oscillatory behavior of solvation forces when separation distance is varied. When you are moving from one maximum of the curve to the next minimum towards right side or in the direction of increasing separation distance, a layer of solution is added to the confined fluid. When you are compressing a confined fluid, it exerts resistance on the approaching surfaces because of its excluded volume/structure. These series of entropic relaxation of solvent (minimum) and quasi layers of solution resisting the approach of the surfaces leads to the oscillatory forces.

6.3.3 Solvent strain for confined solutions

Figure 6.7 shows the density profiles of the solvent that consists of a) Three layers and b) Four layers of solvent for a range of separation distances. This domain actually corresponds to the wall separations of second maxima to third minimum and third maximum to the subsequent minimum from the force profiles as shown in the Figure 6.6. In this domain a layer of solvent has not been added or removed. So we can
analyze the strain on the solvent from a minimum on the forces profile to that of
subsequent maximum. With the increasing separation distance between the walls,
density profiles in Fig 6.7; the amplitudes of peaks near the surfaces are decreasing,
which is due to the entropic relaxation of solvent. This solvent strain imposed by
the approaching surfaces significantly effect the energetics of the overlapping double
layer systems which is demonstrated in the subsequent sections. This layering of the
solvent is what effects the structural forces and makes it oscillatory.

6.3.4 Oscillatory surface charge and electrostatic surface po-
tential

The charge regulation boundary condition on the surface considers that the surface
charge as a result of chemical equilibrium between surface reactive groups and po-
tential determining ions in the solution. As mentioned in the previous chapters the
solvent imparts the structure in to the solution thereby governing the distribution
of ionic species in the solution. In the previous subsection strain on the solvent by
varying wall-separation is shown. This change in the distribution of the solvent re-
sults in the change in the surface concentration of potential determining ions, that
affects surface charge due to the chemical equilibrium 1.18. This effect on the surface
charge and surface potential is shown in Figures 6.8 and 6.9

Figure 6.7 shows that the density profile of solvent experiences changes with the
separation distance. Solvent imparts a structural matrix in the solution which effects
the distribution of the ionic species in the electrolyte solution. With the separation
distance increasing the potential determining ions have more spatial volume to move
over , hence they are not that concentrated near the surface when compared to
the lower wall separations. Hence the surface tends to increase due to the shift in
chemical equilibrium 1.18. It is intersting to see that the increase in surface charge
Chapter 6. Oscillatory Forces and Surface Charge for confined electrolyte Solutions

is not smooth, due to the quasi layered structure of solvent.

A similar influence of the structure is also seen in the surface potential as shown in figure [6.9]. The surface electrostatic potential magnitude decreases with increasing separation distance. The variation in this case also is not smooth but have some oscillations due to solution structure.

6.3.5 pH effects on confined electrolyte solution

pH corresponds to the concentration of PDIs in the solution. Overlapping double layers are influenced by one another and the distribution of PDIs around the surface determine the surface-PDI concentration to react with the surface which can alter the surface charge by equilibrium 1.19. Figure 6.10 shows the variation of surface excess free energy and surface charge dependence on the variation of separation distance for cases with different pH of the solution. Due to the charge regulation, increasing pH decreases the available surface PDI concentration, hence less available reacting species for surface, making the surface more and more negative charged. This is reflected in the figure 6.10, curve corresponding to ph=5.5 has higher negative magnitude of surface charge and the magnitude decreases with decrease in the pH. Surface excess free energy also reflects this dependence. The curve corresponding to higher pH which has usually greater charge, has higher surface excess free energy $\Omega^{ex}$. The forces curves if constructed from this for various cases of pH, show relatively less change and they fall almost on the top of each other. This is due to the dominance of structure over electrostatics. The surfaces considered here are for highly smooth surfaces, hence the magnitude of forces are extremely high. To see the dependence of pH on forces, systems containing rough surfaces or lower packing fraction of solvent could be used.
6.3.6 Effect of packing fraction of solvent

The bulk density of the solvent, which is equivalent to packing fraction of solvent in the electrolyte solution. Figure 6.11 shows the surface/structural forces and surface charge vs wall-separations for three cases of packing fraction of solvent $\rho d_s^3 = 0.6, 0.7$ and 0.8. For cases with higher $\rho d_s^3$, there are larger number of solvent molecules, so when the surfaces are brought closer, there would be greater resistance for fluid’s compression. This clearly is reflected in the greater amplitude of forces for higher bulk density of solvent. Because of the entropic relaxation of solvent for given wall separation there is a shift towards greater wall separation as the bulk density of solvent decreases.

The electrostatics in the system are slightly affected due to the change in the bulk density of solvent, and the slight changes are due to solvent’s structure. With higher packing fraction of solvent the PDIs concentration near the surface becomes less as solvent molecules act as excluded volume barrier hence the greater surface charge. Also, higher bulk density of solvent, more peaks are visible.

6.3.7 Solvent-Solvent interactions and Solvation interactions influence on confined liquids

Solvent-solvent interactions

One of the major drawbacks of classical DLVO is its inability to take account of ion specific interactions like solvation or hydration, surface solution interactions etc. As mentioned in previous chapters we can alter solvent-solvent and ionic solvation interactions with LJ interactions [64–66].

Figure 6.12 shows the dependence of forces and surface charge on solvent solvent
Chapter 6. Oscillatory Forces and Surface Charge for confined electrolyte Solutions

interactions. The $\varepsilon_{\text{sol-sol}}/k_B T$ is used to alter the solvent solvent interactions in the solution. Structural forces are significantly dependent on the solvent structure. When $\varepsilon_{\text{sol-sol}}/k_B T$ values are increased from 0.4 to 1.2, the solvent molecules are drawn into bulk away from the surface. Hence the PDIs can approach the surface and can react with the surface and suppress the surface charge. Hence from the charge figures, the magnitude of the surface charge decreases.

Interactions of PDIs with solvent

The surface charge variation for different wall separations are shown for cases of solvation energies of Potential determining ions are shown in figure 6.13. The trend is opposite to that of solvent - solvent interactions. This is because, PDIs chemically interact with the amphoteric surface, increasing the solvation of PDI, they are drawn into bulk by solvent away from surface. This results in the less density of PDIs near the surface thus increasing the magnitude of surface charge with increasing solvation energies of PDI.

6.3.8 Solvent-Wall interactions effect on confined electrolyte solution

The charged surface is inert in classical DLVO, however, in practice, colloidal surfaces involve in various interactions with the neighboring solution. These surface solution interactions makes the surface- solvophobic or solvophilic. The stability of colloidal dispersions are significantly dependent on these interactions. For single double layer we showed in earlier chapters, surface solvent interactions significantly effect the properties of double layers. Here we show how surface-solvent interactions effect surface forces and surface charge distributions. Figure 6.14 shows the effect of surface solvent interactions on the surface forces and surface charge density.
The structure of solvent predominantly influence the properties of confined electrolyte solutions. When the surface solvent interactions are increased i.e. the surface is changing into more and more solvophilic, the neutral solvent molecules are drawn closer and closer to surfaces through these coulombic interactions. As the system here contains symmetric charge regulating surfaces, the influence of surfaces on either sides of the electrolyte solution is assumed to have same influence on the neutral species solvent. Hence with increasing in the interaction energies of solvent with the wall, the solvent molecules are pushed to the surface regions displacing any potential determining ions near the surface. The structural forces, which significantly depend on the solvent distribution in the solution gets effected as shown in the figure. The solvent-wall interactions increase the amplitude of the peaks of surface forces drastically. This is due to the affinity of the solvent to the surface which makes it harder to expel the layer of solvent when subjected to external compression from the flat walls.

The surface charge density also influenced under solvent-surface interactions, as the potential determining ions are displaced by the solvent molecules at the surfaces with increasing interaction energy. This alters equilibrium 1.19 towards the high surface charge, as the surface reactive species remains un-dissociated. Figure 6.14 shows the same, for higher interaction energy of solvent and surface, magnitude of surface charge is greater.
Chapter 6. Oscillatory Forces and Surface Charge for confined electrolyte Solutions

Figure 6.7. The density profiles of solvent for a) Three layers and b) Four layers, that corresponds to the solvent densities in range of second maximum to corresponding minimum and third maximum to next minimum, in 6.6 i.e. No other quasi layer of solvent is added or removed in this domain.
Figure 6.8. Variation of surface charge with wall separations. The magnitude of the charge decreases with oscillations due to the solvent structure.
Figure 6.9. Oscillatory surface potential in a confined electrolyte solution for increasing wall separations.
Chapter 6. Oscillatory Forces and Surface Charge for confined electrolyte Solutions

Figure 6.10. pH effect on confined electrolyte solutions, a) Surface excess free energy and b) Surface charge as a function of separation distance for the cases pH = 3.5, 4.0, 4.5, 5.0 and 5.5
Figure 6.11. Structural forces and surface charge with separation distance between the charged surfaces for the cases of bulk density of solvent $\rho d_s^3 = 0.6, 0.7$ and 0.8.
Figure 6.12. Structural forces and surface charge with separation distance for solvent-solvent interaction energy $\varepsilon_{\text{sol-sol}}/k_B T$ 0.4 to 1.2.
Figure 6.13. Surface Charge vs separation distance for $\epsilon_{pdi-sol}/k_BT$ varies from 0.2 to 1.2
Figure 6.14. Structural forces and Surface Charge with separation distance for surface solvent interaction energies $\epsilon_{\text{wall-sol}}/k_B T = 2, 4$ and 6.
Chapter 7

Summary and Conclusions

The charge formation at electrolyte interfaces and the properties of EDLs are complex functions of many parameters related to the material properties of the surface and the adjacent solution. The interfacial charge at the IHP is determined by surface chemical reactions (charge regulation) involving the surface reactive groups and components of the solution. All solution components contribute to the final surface equilibria, including species that are not directly participating in the surface reactions, \( \text{(1.18)} \). We show that the precise and detailed solution structure in the vicinity of the interface couples to the charge governing chemical equilibria. The solvent molecules play an important role in establishing this structure due to their exceedingly large number. The solvent contributes to the ionic structure through the excluded volume and LJ interactions. Hence, an accurate physical representation of charged interfaces involving electrolytes requires rigorous statistical mechanical approaches that explicitly account for all solution species and the correlations among them.

The surface chemistry plays an important role for the charge regulating behavior in EDLs. It depends on the material properties of the interface and the composition
of the electrolyte solution in contact with it. This is governed by three parameters: the pI of the surface, the bulk concentration of PDIs (in case of hydronium ions this is conveniently expressed by the pH), and the difference $\Delta pK = pK_- - pK_+$. The situation could be more complicated if more complex surface chemistry is present [40].

The analysis also asserts that the properties of an EDL with surface charge regulation strongly depend on non-Coulombic interactions and correlations in the electrolyte solution. Examples include the bulk solvation as well as non-electrostatic interactions with the EDL interface. The analysis of the solvation and surface interactions explains the fact that different types ions carrying the same charge may lead to a different outcome for the resultant surface charge. It also explains why components that are not directly involved in the surface chemical reactions affect the EDL properties. Hence, the combination of solvation and surface interactions can account for experimental observations that lead to the definition of the Hofmeister series [50,51], electrokinetic results [52], or the ions-specific surfaces forces [53–55]

An important aspect of this study is to provide a framework for proper analysis of experimental data. As discussed above depending on the method one may directly probe the charge at the surface by counting the number of charged groups (using titration) or detect the charge at the shear plane (using electrokinetic methods). These could be and often are very different. Civilized DFT allows to distinguish between these cases and provides explanation for the difference based on rigorous statistical mechanical arguments.

The solvent-solvent interactions do no directly involve and charged species and yet, their effect is significant. The solvent molecules occupy a considerable fraction of the Stern layer and hence, determine its overall charge. A linear relationship between the surface potential and the energy parameter for the Lennard-Jones solvent attraction is observed.
Chapter 7. Summary and Conclusions

The solvation of the potential determining ions also affect the properties of the electric double layers. The main factor that plays a role in this case is the surface reaction. In the presence of additional and chemically inert ionic species, the charge density in the Stern layer exhibits a minimum with the variation of the potential determining ions solvation strength.

The positive non-potential determining ions interaction with the solvent also has an effect on the properties of the electric double layer. Depending on the strength of the solvation interactions, these ions accumulate in different quantities in the Stern layer and thus, determine its charge. The positive ions, while chemically inert with respect to the surface, may serve as an excluded volume/electrostatic barrier for the potential determining ions and hinder their access to the interface. Hence, the positive ion solvation can indirectly affect the surface charge.

The solvation of the negative ions may have a dramatic effect on the electric double layer. When poorly solvated these ions accumulate the Stern layer and add more negative charge to an already negative surface. A strong solvation of the negative ions, however, eliminates this effect.

The non-Coulombic interactions of the potential determining ions with the surface obviously have an impact on the charged interface properties. Their absence, or presence in the Stern layer governs the surface charge by means of the regulation reaction. In addition they compete with the rest of the ionic species for space in the Stern layer, which also affects the system properties. As the number of potential determining ions in the Stern layer becomes high enough they may change the surface charge polarity by shifting the chemical equilibrium. In our example above, this means that the surface obtains the same positive polarity as the potential determining ions. A somewhat unexpected observation is that as the number of positive potential determining ions increases even further it is accompanied by an increased incorporation on negative counterions in the Stern layer.
Chapter 7. Summary and Conclusions

The adsorption of positive, non-potential determining ions creates a barrier for the same charged potential determining ions and prevent them from chemically interacting with the surface. This effectively increases the surface charge. The charge in the Stern layer however, becomes more positive with the adsorption and the potential distributions switch from negative to positive. The surface potential exhibits a complex and non-monotonic behavior.

The Lennard-Jones driven adsorption of negative ions occurs (for the selected set of parameters) at a negative surface. As the number of negative ions in the Stern layer increases so does the number of positive ions, although to a lesser extent. This resembles the potential determining ions case where the adsorption of positive ions at a positive interface always leads increased adsorption of negative ions. Hence, it may be concluded that whenever ions are adsorbed at a surface that has the same charge sign, some counterions are always incorporated into the Stern layer because of the strong electrostatic attraction that acts upon them.

Non-Coulombic interactions with the charged surface in an electric double layer have a significant impact on its properties. A proper account of these interactions is a necessary step towards explaining the wide variations in attributes of charged interfaces that are otherwise identical form purely electrostatic perspective.

The density distributions of the ions near the charged wall are primarily driven by their Coulombic charge, and the presence of the solvent molecules. The charge of their counterion partners, also has an effect, albeit smaller.

The combination of Coulombic and non-Coulombic interactions specify the local density distributions of all species including the potential determining ions. The local density of the latter affects the surface chemical equilibrium (i.e., the surface charge and potential). The surface electrostatics in turn determines the density distributions of all charged ions in the solution.
Chapter 7. Summary and Conclusions

In summary we believe that civilized statistical mechanical approaches (such as DFT) together with a proper account for all chemical equilibria at the EDL boundary offers the best theoretical background for modeling and analysis of charged interfaces that involve electrolyte solutions. The simple model presented in this work can be extended to include more components and/or more sophisticated functionals. This is a strategy that allows obtaining further insights into the properties of charged colloidal systems.
Chapter 8

Future Work

The studies presented in this dissertation can be extended to various cases which are listed in this following chapter.

The classical DFT system presented in this thesis is an equilibrium system with a system of grand thermodynamic ensemble, this can be extended to a non-equilibrium system, that can be used to explore time dependent characteristics of electric double layers \cite{116,117,17,84}. This will allow solving problems pertinent to surface reactions and solute diffusion

Corrosion is a process when a metallic surface oxidizes due to the chemical reaction between the surface and the oxygen present in the atmosphere or moisture. The charged metal and aqueous environment that surrounds it constitutes an electric double layer. This CDFT based reactive surface model presented in this thesis is convenient to study different environments and ionic specific effects that influence corrosion process. A multi-scale modeling method can be developed on our current model to study sub processes in corrosion like its propagation and dependence of environmental factors etc., \cite{118,119,120}
Chapter 8. Future Work

The confined electrolyte solution presented has identical charge regulating walls surrounding it. This model can be extended to asymmetrical surfaces with separate charge regulation boundary condition for each surface. The non-coloumbic interactions also could be asymmetrical, i.e. one of the surface could be solvophilic and the other solvophobic. The distribution of electrolyte solutions under these conditions could bring more physical insights and could incorporate more diverse physical systems.

Though the solvent is explicit in this model, we still have dielectric constant of the solvent to be constant. This in reality may not be true, [57]. The incorporation of species density based dielectric permittivity could bring more physical insights, if the current systems are used to study phase transitions.

Electric double layers have significant role in the energy systems. This thesis already captured the deviation of ionic distributions from Poisson-Boltzmann approaches and having an explicit solvent model coupled with charge regulation shows different distribution of ionic species. Hence solvation, ion-packing and other phenomena could significantly effect the current understanding of capacitive electrodes [121]. The capacitance of the pores or thin films could be studied using our analysis presented for confined electrolyte solutions.
Appendices
Appendix A

Reduced units

The Classical DFT computations are performed using Tramonto [74]. The reduced units of different quantities used in this study are briefly illustrated in this appendix.
## Appendix A. Reduced units

Table A.1. Dimensionless quantities and corresponding scaling parameters that are used in classical density functional theory calculations from Tramonto.

<table>
<thead>
<tr>
<th>Dimensionless quantity</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distances</td>
<td>$L/d_{\text{ref}}$, All the parameters involving distances are scaled to $d_{\text{ref}}$.</td>
</tr>
<tr>
<td>Particle sizes</td>
<td>$d_i/d_{\text{ref}}$, $d_i$ is the particle diameter, $d_{\text{ref}}$ is reference distance, in case of species with multiple components, $d_{\text{ref}}$ will be taken by particle diameter of the first component.</td>
</tr>
<tr>
<td>Density</td>
<td>$\rho/d_{\text{ref}}^3$ Density profiles of the species are scaled to $d_{\text{ref}}$.</td>
</tr>
<tr>
<td>Interaction energy($\epsilon$)</td>
<td>$\epsilon/k_B T$ Scaled to Thermal energy $k_B T$.</td>
</tr>
<tr>
<td>Pressure</td>
<td>$pd_{s}/k_B T$ Pressure developed due to confinement of fluids</td>
</tr>
<tr>
<td>Force</td>
<td>$fd_{s}^{3}/k_B T$ Forces developed due to confinement of fluids</td>
</tr>
<tr>
<td>Energy</td>
<td>$\Omega d_{s}^{2}/Ak_B T$ Scaled to Thermal energy</td>
</tr>
<tr>
<td>Charge</td>
<td>$\sigma d_{s}^{2}/e$</td>
</tr>
</tbody>
</table>
Appendix B

Bulk charge densities for multivalent electrolytes

There are many approaches to study the underlying influence of electric double layers by multivalent electrolytes in an electrolyte solution. As the valencies of components of electrolyte species are additional parameters to investigate as comparison with rest of those used in this dissertation, and to present the studies in an elegant manner, we employed the following approach.

The decay of the structural effects of the solution is determined by Debye Screening length $\lambda_D$. This Debye length is mainly dependent on the Ionic strength of the solution. We fix the Ionic strength of the solution for different cases of their valencies.

So, For an electrolyte solution, of charges $+m$ and $-n$ as the valencies of Positive and negative electrolyte species in the solution, and the Ionic strength is given by $I$, the four component model of our EDL which consists of Potential Determining Ions ($PDI$), Solvent ($sol$), Non-PDI Postive ions ($pos$), Non-PDI Negative ions ($neg$).
Appendix B. Bulk charge densities for multivalent electrolytes

The Ionic strength of solution is given by,

\[ \frac{1}{2}(\rho_{PDI} \times (+1)^2 + \rho_{sol} \times (0)^2 + \rho_{pos} \times (+m)^2 + \rho_{neg} \times (-n)^2) = I \]  \hspace{1cm} (B.1)

At Bulk, the charge neutrality of the fluid is always maintained,

\[ \rho_{PDI} \times (+1) + \rho_{sol} \times (0) + \rho_{pos} \times (+m) + \rho_{neg} \times (-n) = 0 \]  \hspace{1cm} (B.2)

The Potential determining ions are equivalent to the Hydronium ions that involve in the chemical equilibrium with the surface dissociating groups. The bulk concentration is determined by pH of the solution. Hence,

\[ \rho_{PDI} = 10^{-pH} \]

Hence, Substituting this in equations [B.1] and [B.2]

\[ m^2\rho_{pos} + n^2\rho_{neg} = 2I - \rho_{PDI} \]  \hspace{1cm} (B.3)

\[ m\rho_{pos} - n\rho_{neg} + \rho_{PDI} = 0 \]  \hspace{1cm} (B.4)

\[ m^2\rho_{pos} + n^2\rho_{neg} = 2I - 10^{-pH} \]  \hspace{1cm} (B.5)

\[ m\rho_{pos} - n\rho_{neg} + 10^{-pH} = 0 \]  \hspace{1cm} (B.5)

On solving for the bulk densities of the positive and negative non-PDIs, we get

\[ \rho_{pos} = \frac{2I - (n + 1)10^{-pH}}{mn + m^2} \]  \hspace{1cm} (B.6)

\[ \rho_{neg} = \frac{2I - (n + 1)10^{-pH}}{n(n + m)} + 10^{-pH} \]  \hspace{1cm} (B.7)
Appendix C

Electrostatic surface potential dependence on solvent diameter for spinodal phase separation systems

The effect of the explicit molecular structure on the properties of charge interfaces is shown in Figure 2.1 of Chapter 2. The surface charge effect on the solvent diameter is presented in that analysis. This dissertation is centered on silica like charged-surface, i.e. the surface characteristic properties are considered to mimic silica surfaces. This appendix presents a cDFT computation of the surface potential of the $Al_2O_3$/Water interface to study the solvent diameter effect on the surface potential. The surface chemistry parameters, used in the computation, are $\Gamma = 10^{18}m^{-2}$, $pI = 8$, $\Delta pK = pK–pK+ = 4$, $pH = 5$. The solvent contribution is gradually introduced by changing the diameter of the solvent molecules, $ds$, from zero to that of the participating ions, $d$. Effectively this means that we are switching form a com-
Appendix C. Electrostatic surface potential dependence on solvent diameter for spinodal phase separation systems

Figure C.1. Surface potential of an EDL as a function of the solvent molecular diameter. The different curves are for different values of the LJ parameter $\epsilon_{ij}$, which starts at zero (top curve) and increases by increments of $0.1 \, k_B T$, with the exception of the dashed curve, which is for $\epsilon_{ij}/k_B T = 0.76$ (see the text). The dot corresponds to the critical point. The surface characteristics are $pI = 8$, $\Delta pK = 4$ and $pH = 5$.

pletely structureless solvent, to one where the solvent molecules contribute to the physical properties with their excluded volume and other possible non-Coulombic interactions. The surface potential, shown in [C.1] is a strong function of the solvent diameter, and also of the strength of the non-Coulombic interactions. The different curved correspond to different values of the LJ parameters $\epsilon_{sol-sol}$, starting from zero (top curve) and increasing to $1.2 \, k_B T$ in the increments of $0.1$. The overall fluid density increases with the solvent diameter and in the presence of attractive LJ interaction if exhibits a spinodal phase separation as indicated by the dotted line in the figure. While not truly physical, this result clearly shows that not taking the explicit solvent molecular structure leads to a physically meaningless result. Hence,
Appendix C. Electrostatic surface potential dependence on solvent diameter for spinodal phase separation

A proper account of the properties of charged interface requires a molecular model of the fluid structure, coupled with the actual surface chemistry at the liquid/solid interface.
References


References


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References


References


References


References


References


References


References


References


References


References


References


References


[184] “Supplemental Material.”


References

dependence of the double layer capacitance for the restricted primitive model
of an electrolyte solution from a density functional approach,” The Journal of

[195] T. Yamaguchi and S. Koda, “Bimodal dielectric relaxation of electrolyte solu-
tions in weakly polar solvents,” J. Chem. Phys., vol. 141, no. 24, p. 244501,
2014.


[197] D. J. Prakash, “Ion size effects on the properties of charge regulating electric
double layers,” 2017.

surface forces in thin liquid films: Influence of multivalent coions and extended

[199] G. Trefalt, I. Szilagyi, and M. Borkovec, “Poisson–boltzmann description of
interaction forces and aggregation rates involving charged colloidal particles
in asymmetric electrolytes,” Journal of colloid and interface science, vol. 406,

and double layer forces acting between charged particles in solutions of like-
charged polyelectrolytes and monovalent salts,” Soft matter, vol. 13, no. 18,

solution of macromolecules,” The Journal of Chemical Physics, vol. 22, no. 7,

forces in the presence of electrostatic double layer repulsion,” Physical review

[203] M. Moazzami-Gudarzi, T. Kremer, V. Valmacco, P. Maroni, M. Borkovec, and
G. Trefalt, “Interplay between depletion and double-layer forces acting between
charged particles in solutions of like-charged polyelectrolytes,” Physical review

and origin of repulsive hydration forces,” Nature, vol. 306, no. 5940, p. 249,
1983.