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Hydration Forces

HYDRATION FORCES

A STUDY OF SHORT-RANGE INTERACTIONS USING ATOMIC FORCE MICROSCOPY

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SUMMARY

The hydration force was introduced after the observation that clays and lipid bilayers swell spontaneously or repel each other in aqueous solutions, and silica dispersions and other colloidal particles remain stable in concentrated salt solutions, where one would expect that, due to the screened repulsive electric double layer, the attractive van der Waals will dominate resulting in aggregation of the particles. These ‘additional’ forces found in aqueous solutions have become known as ‘hydration forces’. The short-range interactions, that are not described by the DLVO theory, can be repulsive or attractive, and decay exponentially over 1-2 nm and can be oscillatory. The latter arise when water molecules are induced to order or ‘structure’ into quasi-discrete layers between two surfaces. Despite limited available theoretical models to describe the hydration force, its general form can be expressed by a monotonically- and an oscillatory decaying contribution.

Experimental studies in salt solutions have reported that the hydration force is both ion- and surface specific. However, it remains unknown how the oscillatory and the monotonic contribution to this force are affected by specific ions and how and if their contributions are correlated. In this work, I measured the hydration forces in a large variety of conditions and looked into both contributions of the hydration force. The general form of the experiments is as follows: forces were measured between a sharp AFM tip and a surface (either mica or silica) in an aqueous solution over 5 nm separation. Salt solutions of different cation types were studied and the ambient temperature was varied. The obtained forces were fitted to an empirical equation that consists of an oscillatory and a monotonic contribution, enabling us to study the effect of the environmental condition on both contributions to the force.

In **Chapter 2**, I will give more information on AFM and on the analysis procedure of the experimental data. In **Chapter 3** I show our study on the hydration force at mica surfaces in the presence of different types of monovalent cations (1+). I show that oscillatory hydration forces, as a result of the packing of water molecules, are stable in the absence of added ions. I show that both contributions to the force are affected by the

type of cation present in solution. The monotonic contribution to the hydration force decreases in strength with decreasing the bulk hydration energy of the cation in solution, leading to a transition from an overall repulsive to an attractive force. The oscillatory part in contrast plays a binary character, being hardly affected by the presence of strongly hydrated cations but becomes completely suppressed in the presence of weakly hydrated cations, which agrees with complementary Molecular Dynamics simulations.

Chapter 4 focusses on the effect of different types of divalent cations (2+) on the hydration force at mica surfaces. Here I show that the oscillatory hydration force remains stable in the presence of different types of divalent cations, unlike what was found for the monovalent cations. While the oscillatory force is mostly unaffected, the monotonic contribution is attractive at intermediate salt concentrations, but becomes slightly repulsive at higher concentrations.

Not only ions in solution but also the surface itself influences the interaction forces. In **Chapter 5** I show a study on the effect of the surface on the hydration force, where experimental data is presented that is acquired at mica and silica surfaces. Mica is atomically smooth after cleavage, while the thermally grown silica surfaces used in this study are amorphous. I show that the oscillatory hydration force is not only stable at atomically smooth surfaces such as mica, but that it is found at silica surfaces as well. The monotonic contribution to the force does show minor variations between the two surfaces but generally, the hydration forces at mica and silica surfaces show to be remarkably similar, that points to fundamentally similar hydration interactions at both surfaces.

In the last experimental chapter, **Chapter 6**, a study on the effect of temperature on the hydration force is presented where I show that the oscillatory hydration force is remarkably stable, even in ambient temperatures of 65°C. Additionally, the monotonic contribution of the force measured in purified water becomes more and more attractive upon increasing the temperature, which is more pronounced in the presence of salts. Lastly, in **Chapter 7** I summarize my conclusions and present recommendations for future work.

SAMENVATTING

De hydratatiekracht werd geïntroduceerd na de waarneming dat klei-deeltjes en lipidebilagen spontaan zwellen of elkaar afstoten in waterige oplossingen, siliciumsuspensies en andere colloïdale deeltjes stabiel blijven in geconcentreerde zoutoplossingen, waar men zou verwachten dat vanwege de afgeschermded repulsieve elektrische dubbellaag, de attractieve vanderwaalskracht zou domineren en zou leiden tot de aggregatie van de deeltjes. Deze ‘extra’ krachten in waterige oplossingen staan bekend als ‘hydratiekrachten’. De kortereafstandsinteracties, die niet worden beschreven door de DLVO-theorie, kunnen repulsief of attractief zijn, en vervallen exponentieel over 1-2 nm. Daarbij kunnen de krachten oscillerend zijn. Dat laatste ontstaat wanneer watermoleculen worden geïnduceerd om te ordenen of te 'structureren' in quasi-discrete lagen tussen twee oppervlakken. Ondanks dat er geen beschikbare modellen zijn om de hydratatiekracht te beschrijven, kan zijn vorm worden uitgedrukt door een monotone en een oscillerende vervallende bijdrage aan de totale kracht.

Experimentele studies in zoutoplossingen hebben aangetoond dat de hydratatiekracht kan worden beïnvloed door de grootte van de ionen in oplossing en door het type oppervlak waarop de krachten gemeten worden. Het blijft echter onbekend hoe de oscillerende en de monotone bijdrage aan deze kracht worden beïnvloed door specifieke ionen en hoe en of deze bijdragen zijn gecorreleerd. In dit werk heb ik de oscillerende hydratatiekrachten in een grote verscheidenheid van omstandigheden gemeten en beide bijdragen van de hydratatiekracht bekeken. De algemene vorm van de experimenten is als volgt: krachten werden gemeten tussen een scherpe AFM-punt en een oppervlak (ofwel mica of silica) in een waterige oplossing over een afstand van 5 nm. Zoutoplossingen van verschillende kationentypes werden bestudeerd en de omgevingstemperatuur werd gevarieerd. De gemeten krachten werden beschreven met een empirische vergelijking (bestaande uit een oscillerende en een monotone bijdrage) waardoor ik het effect van de omgevingsomstandigheden op beide bijdragen van de kracht kon bestuderen.

In **hoofdstuk 2** geef ik meer informatie over AFM en over de analyseprocedure van de experimentele gegevens. In **hoofdstuk 3** laat ik onze studie naar de hydratiekracht op mica-oppervlakken in de aanwezigheid van verschillende soorten monovalente kationen ($1+$) zien. Hier toon ik aan dat de oscillerende hydratiekracht, als gevolg van de stapeling van watermoleculen stabiel is in afwezigheid van toegevoegde ionen. Ik beschrijf de totale krachtgradiënt door een oscillerende en een monotone bijdrage en laat zien dat beide worden beïnvloed door het type kation dat in oplossing aanwezig is. De monotone bijdrage aan de hydratiekracht neemt af in sterkte met het verminderen van de bulkhydratie-energie van het kation in oplossing, hetgeen leidt tot een overgang van een totale repulsieve naar een attractieve kracht. De oscillerende bijdrage heeft daarentegen een binair karakter en wordt nauwelijks beïnvloed door de aanwezigheid van sterk gehydrateerde kationen, maar wordt volledig onderdrukt in de aanwezigheid van zwak gehydrateerde kationen, wat overeenkomt met complementaire Molecular Dynamics-simulaties.

Hoofdstuk 4 richt zich op het effect van verschillende soorten divalente kationen ($2+$) op de hydratiekracht op mica-oppervlakken. Hier laat ik zien dat de oscillerende hydratiekracht stabiel blijft in de aanwezigheid van verschillende soorten divalente kationen, in tegenstelling tot wat werd gevonden bij de monovalente kationen. Hoewel de oscillerende kracht meestal niet wordt beïnvloed, is de monotone bijdrage attractief bij gemiddelde zoutconcentraties, maar wordt deze bij hogere concentraties enigszins repulsief.

Niet alleen ionen in oplossing, maar ook het oppervlak zelf beïnvloedt de interactiekrachten. In **hoofdstuk 5** laat ik een studie zien naar het effect van het oppervlak op de hydratiekracht, waarbij experimentele resultaten worden getoond die zijn verkregen op het oppervlak van mica en silica. Mica is na splijting atomair glad, terwijl de thermisch gegroeide silica-oppervlakken, die in deze studie worden gebruikt, amorf zijn. Ik laat zien dat de oscillerende hydratiekracht niet alleen stabiel is op atomair gladde oppervlakken zoals mica, maar dat deze ook wordt gevonden op silica-oppervlakken. De monotone bijdrage aan de kracht vertoont variaties tussen de twee oppervlakken, maar in het algemeen blijken de

hydratiekrachten op het mica- en silicaoppervlak opmerkelijk vergelijkbaar te zijn, hetgeen wijst op fundamenteel vergelijkbare hydratie-interacties op beide oppervlakken.

In het laatste experimentele hoofdstuk, **hoofdstuk 6**, wordt een onderzoek naar het effect van temperatuur op de hydratiekracht gepresenteerd, waarin ik aantoon dat de oscillerende hydratiekracht opmerkelijk stabiel is, zelfs bij omgevingstemperaturen van 65°C. Bovendien wordt de monotone bijdrage van de kracht gemeten in water steeds attractiever bij het verhogen van de temperatuur, wat nog duidelijker is in de aanwezigheid van zouten. Ten slotte vat ik in **hoofdstuk 7** mijn conclusies samen en geef ik aanbevelingen voor toekomstig werk.

TABLE OF CONTENTS

INTRODUCTION	1
1.1 INTERACTION FORCES	2
1.2 DESCRIBING INTERACTION FORCES	3
1.3 SHORT-RANGE INTERACTION FORCES	6
1.4 MONOTONIC HYDRATION FORCES	11
1.5 AIM OF THIS THESIS.....	15
1.6 REFERENCES	17
METHODS.....	21
2.1 ATOMIC FORCE MICROSCOPY	22
2.2 EXPERIMENTAL PROCEDURE.....	25
2.3 DATA ANALYSIS	27
2.4 VAN DER WAALS INTERACTION.....	31
2.5 CONCLUDING REMARKS	39
2.6 SUPPLEMENTARY INFORMATION.....	40
2.7 REFERENCES	44
THE EFFECT OF ALKALI CATIONS AND PH	47
3.1 INTRODUCTION	48
3.2 METHODS.....	50
3.3 RESULTS AND DISCUSSION	52
3.4 CONCLUSION	66
3.5 SUPPLEMENTARY INFORMATION	67
3.6 REFERENCES	83
THE EFFECT OF DIVALENT CATIONS	91
4.1 INTRODUCTION	92
4.2 METHODS.....	94
4.3 RESULTS AND DISCUSSION	95
4.4 CONCLUSION	113
4.5 SUPPLEMENTARY INFORMATION	115
4.6 REFERENCES	124

THE EFFECT OF THE SUBSTRATE.....	129
5.1 INTRODUCTION	130
5.2 METHODS.....	132
5.3 RESULTS	134
5.4 DISCUSSION	145
5.5 CONCLUSIONS.....	150
5.6 SUPPLEMENTARY INFORMATION.....	152
5.7 REFERENCES	159
THE EFFECT OF ELEVATED TEMPERATURE	165
6.1 INTRODUCTION	166
6.2 METHODS.....	168
6.3 RESULTS	169
6.4 DISCUSSION	175
6.5 CONCLUSIONS.....	178
6.6 SUPPLEMENTARY INFORMATION.....	180
6.7 REFERENCES	184
CONCLUSIONS AND OUTLOOK.....	187
7.1 CONCLUSIONS.....	188
7.2 OUTLOOK	190
7.3 REFERENCES	192
ACKNOWLEDGMENT	193

INTRODUCTION

1.1 Interaction forces

As is true for most sciences, the first considerations of nonreligious forces were initiated by the Greeks. Initially, two fundamental forces were proposed, as still forms the basis of many stories in books and movies: love and hate (by Empedocles, c. 490-330 BC).¹ The first brings things or people together, and the latter repels them apart. It was observed that the attraction and repulsion was not only found in romantic stories but as well in matter, such as in magnetics. Magnets could be used to find iron, when different bodies were rubbed against each other, sparks would show up in addition to an attraction or repulsion. These observations remain wonders to those who observe them for the first time, but now, in the 21st century, we are able to describe and explain most of these phenomena.

In this thesis we consider interaction forces that dominate in a liquid environment, in my view, the most interesting liquid environment there is: water. Water is clearly the most abundant fluid on earth. For those who like numbers, 71% of the Earth's surface is water-covered, the oceans hold 96.5% of all water. Without water there is no life possible on earth. It is not only an important solvent, it is also a very interesting one. The water molecule is quite simple, consisting of only one oxygen and two hydrogen atoms. It is one of the first molecular formula everyone learns in school: H_2O . Any other substance of such a small size would not be a liquid, and therefore would not run from your morning shower. Water is remarkable due to its unique properties: it can both donate and accept two hydrogen bonds. Hydrogen bonds are electromagnetic attractions between a slightly positive charged hydrogen-atom in a water molecule and a lone electron pair on the oxygen of another. As a result of, on average, four of such bonds, water molecules form a tetrahedral network that is remarkably strong. This network is the reason for many of the anomalies of water such as its high density, high surface tension, high viscosity, and low compressibility, high boiling point etc. This strong hydrogen bonded network is very dynamic in nature which leads to water's ability to solvate ions (charged particles) and other solutes. In this thesis I will describe interaction forces between two bodies in a water environment, mostly in which ions are solvated, where I hope you will learn that the addition of ions results in interesting phenomena.

1.2 Describing interaction forces

In science we like to think that we understand a phenomenon once we can describe the observation in a mathematic matter. The theory of Derjaguin, Landau,² Verwey and Overbeek³ (DLVO) is the dominant theory used in ‘interaction-science’. According to the DLVO theory, the pressure between two bodies is the sum of two interactions: the attractive van der Waals interaction and the double-layer component (Figure 1.1).

Figure 1.1. An example of the total interaction force described by the DLVO theory between two negatively charged bodies in solution. The blue line represents the electric double layer force, which is repulsive due to the pressure between the particles as a result of the enhanced ion concentration.

The first acts between all atoms and molecules and quickly vanishes at longer distances between interacting bodies. The van der Waals force differs from covalent and ionic bonding in that they are caused by correlations in the fluctuating polarizations of nearby particles. Just remember that this force is typically an attractive interaction between bodies in a medium (such as water) at short distances (red line in Figure 1.1). In this work I shall describe attractive interactions as negative forces and repulsive interactions as positive forces. If only the van der Waals

force would operate, we can therefore expect that all particles stick together. Clearly this does not happen, because particles suspended in water, or any other liquid of high dielectric constant, are usually charged which prevents coalescence by repulsive ‘electrostatic’ forces (positive forces).¹

The charging of surfaces in a liquid can be the result of different mechanisms such as the ionizations or dissociation of surface charges ($-\text{COOH} \rightarrow -\text{COO}^- + \text{H}^+$), or by the adsorption or binding of ions. As a result of the surface charge, or surface potential, counterions (ions that accompany charges to maintain electric neutrality) will be attracted from the solution towards the surface. As schematically shown in Figure 1.2: positively charged ions (cations) will be attracted to a negatively charged surface. In equilibrium, the surface charge is balanced by the oppositely charged ions. This region near the surface, where a high concentration of counterions is found, is called the electric double layer (EDL).

The EDL can be divided into two regions. Ions in the region closest to the charged wall form the so-called Stern layer. The region adjacent to the Stern layer is the diffuse layer and contains the counterions and co-ions. The concentration of counterions and co-ion decays as a function of distance from the surface, as shown in Figure 1.2b. The potential of the surface has a maximum value at the surface and is defined to be 0 in the bulk. The concentration profile of the ions follows an exponential decay according to the Gouy-Chapman model. An exponential decay is a mathematic description with a so-called ‘decay-rate’, in this case κ (Debye parameter) with the quantity length $^{-1}$. The Debye length, κ^{-1} , is the characteristic length of this decay function. It provides insight into the relevant length scales of the interactions and the concentration profiles. If there are more ions present in the solution, the double layer will be smaller due to the fact that the ions in solution can compensate the surface charge and potential. Therefore, by changing the salt concentration, the thickness of the double layer can be tuned.

Figure 1.2. Schematic of the electric double layer (EDL) model. a) Schematic of accumulation of counterions near a negatively charged surface. b) Ion concentration along the distance from the negatively charged surface. Counterion concentration builds up inside the EDL, at large separations it reaches a plateau in the bulk fluid.

So, there is a charged surface, with counter- and co-ions in solution that compensate the potential of the surface. How does overlap of the double layers of two surfaces, as schematically shown in Figure 1.1, results in a repulsive force? Contrary to intuition, the origin of the repulsive force between two similarly charged surfaces in a solvent containing

counterions and/or added electrolyte ions is entropic (osmotic), and not electrostatic. The electrostatic interaction is actually attractive. Upon dissociation of counterions from a surface, the double layer is maintained by the repulsive osmotic pressure between the counterions which forces them away from the surface and from each other to increase their configurational entropy. When bringing two surfaces together, the counterions are forced back onto the surfaces against their preferred equilibrium state, against their osmotic repulsion but favored by the electrostatic interaction. The former dominates; hence this contribution is repulsive.

1.3 Short-range interaction forces

The DLVO theory is a continuum theory, which means that it does not describe or consider the discrete nature of the solvent or the ions. This work very well up to the first few nanometers from the surfaces, where the liquid film is only a few solvent molecules thick. The interactions that cannot be described using this theory, and that dominate in the first nanometer from the surfaces, are therefore termed non-DLVO forces. These forces are the focus of this thesis. The short-range interactions, that are not described by the DLVO theory, can be repulsive or attractive, which can be described monotonically or even oscillatory. The latter arise when liquid molecules are induced to order or ‘structure’ into quasi-discrete layers between two surfaces.

1.3.1. Oscillatory forces

Oscillatory forces mainly have a geometric origin, the force depends on the shape and size of the liquid molecules. To understand how this force arises, let us first consider liquid molecules and their order at one single, isolated surface. The surface, or wall, takes away one degree of freedom for the motion of the liquid molecules. Starting from the surface, the molecules are most likely to be found at distances $x = (n - \frac{1}{2}) * \sigma$ (where n is the number of molecules and σ their size), while the correlation strongly decreases after a few layers.

The red line in Figure 1.3a shows the density distribution of the molecules, which oscillates with a periodicity of the size of the molecules that decays away from the wall. When bringing the two surfaces together,

the density distribution of both surfaces' overlaps (Figure 1.3b). This results in an alternating increase and decrease of the total density; this modulation of the total density causes the pressure on the surfaces to oscillate as a function of distance. These pressure oscillations can be measured as oscillatory solvation forces. It is important to realize that the solvation force only arise because of the disruption or change of ordered liquid molecules during the approach of a second surface.

Figure 1.3 a) Schematic representation of n spherical liquid molecules packed near a surface/wall. The liquid has a quasi-discrete structure and its density is oscillatory decaying as a function of distance x from the surface. b) Solvent molecules confined between two walls.

The first oscillatory forces were measured in a relatively large molecular sized organic liquid between two surfaces using a surface force apparatus ((SFA), which is an instrument where interaction forces between two surfaces can be measured as they are brought together).⁴ This was quite exciting since it was the first direct evidence that the interfacial liquid is not bulk-like. Real systems are of course more complicated than what is schematically depicted in Figure 1.3. The liquid molecules are non-spherical and interact via anisotropic orientation-dependent potential both with each other and with the surfaces.

The packing of solvent molecules is affected by the interactions of the solvent with the surface. When the interactions between the solvent and

the wall is strong, the correlations will be stronger as well. As a result, the amplitude (maximum) of the density-oscillation is higher and it will extend over larger distances. Furthermore, the shape and size of the solvent molecules is of importance. Irregularly shaped chain molecules with side groups or branching lack a symmetry axis and so cannot easily order into layers. Figure 1.4 shows the comparison of the forces measured between smooth surface in a solvent composed of linear solvent molecules and in a solvent of branched, irregularly shaped solvent molecules. In the presence of the linear solvent molecules, the force shows a pronounced oscillatory character at short separations.

Figure 1.4. Measured force between smooth surfaces across liquid alkanes (organic molecules), where the linear alkane solvent results in an oscillatory solvation forces, while the force is monotonic in the presence of the branched alkane. (Data adapted from Christenson et al., 1987, and Gee and Israelachvili, 1990).⁵

The amplitude of the oscillation increases with decreasing distance since the layering is more pronounced near the wall (see Figure 1.3). The

schematic molecular picture is given in the top part of the figure. In the presence of branched solvent molecules (as schematically shown in the picture in the lower part of Figure 1.4), the oscillatory contribution to the force is not measured but a monotonic interaction force is found. The attractive van der Waals contribution is given in this figure as well, shown by the dotted line. This is good to remember; indeed, the short-range force does not follow what is predicted by the DLVO interactions: it is either oscillatory or monotonic repulsive or attractive at short distances (non-DLVO).

However, we are interested in aqueous solutions where the solvent (water) is far more complex due to the fact that water molecules have a strong, orientation dependent interaction with each other plus, dissolved salts adsorb onto the surfaces and interact with the water molecules depending on their specific properties, which we will discuss later in this story. But first let us discuss the packing of water molecules.

1.3.2 Oscillatory hydration forces

This might seem odd, at least to me it was at first: the packing of water molecules near walls. As you have learned above, the hydrogen bonded network of water is strong but very dynamic in nature, and as a result it can adapt itself easily to, for example, the solvation of ions. You must have noticed that aspirin and kitchen salt can easily be dissolved into a glass of water: after a bit of shaking, there are no more particles visible – the solute is dissolved. Despite this dynamic nature of water molecules, experimentalists were able to measure oscillatory forces in aqueous solutions between smooth surfaces.⁶ Figure 1.5 shows their experimental data: an oscillatory force is measured with a periodicity close to the size of a water molecule: 0.25 nm. This indicates that layering is indeed the result of the packing of the solvent: the water molecules.

The oscillatory line in this figure is there to guide the eyes, the points are the actual measured data points. The instrumentation of that time was not able to measure the entire force profile of the oscillatory force in aqueous solutions. The oscillatory forces profile measured in aqueous solutions was termed the oscillatory hydration force (the solvent is hydrating the surface). It is important to point out that the oscillatory hydration force profile was only detected in force measurements if there

are ions present. As a result of that, it was believed that the oscillatory hydration force is the result of the dehydration of the hydrated ions.⁷ What do we mean by hydrated ion? Ions are charged particles. The polar water molecules orientated themselves towards ions to compensate its charge.

Figure 1.5. Measured short-range force between two smooth surfaces in aqueous salt solutions (0.01 M KCl). The dashed line shows the expected DLVO interaction. (Data adapted from Israelachvili and Pashley, 1983).⁶

Positively charged ions, cations, are surrounded by water molecules that orientate their partially negatively charged oxygen atoms towards the cation. Oppositely, negatively charged ion, anions, are surrounded by water molecules that point their partially positively charged hydrogen towards the ions. These layers of water molecules around ions are termed hydration shells. The size of the ion is correlated to the charge density, and therefore to the amount of water molecules that are orientated towards the ion: the smaller the ion, the higher the charge density, the more water

molecules are orientated towards the ions and therefore, the more hydrated the ion.

So, it was concluded that there were ions needed in order to observe the oscillatory hydration force. However, more recent experiments (*e.g.* x-ray diffraction)⁸⁻¹⁰ have reported an oscillatory density profile of water molecules near smooth surfaces in the absence of added salts. But from the older SFA experiments it was clear that ions have an important effect on the oscillatory hydration force. Clearly there are discrepancies between the interpretations based on the force measurements and the more recent experimental findings on the structure of the solid-liquid interface.

Before I will discuss more about the effect of ions on the hydration forces, first, I like to point out that the oscillatory force is not necessarily symmetric at $F = 0$, but is often superimposed on a monotonic force, as is also observed in Figure 1.5: the overall oscillatory force is positive, and therefore repulsive. This (monotonic) hydration force is one of the most discussed forces in literature.^{11, 12}

1.4 Monotonic hydration forces

The hydration force was introduced after the observation that for example, clays¹³ and lipid bilayers^{14, 15} swell spontaneously or repel each other in aqueous solutions, and silica dispersions¹⁶ and other colloidal particles¹⁷ remained stable in concentrated salt solutions, where one would expect that, due to the screened repulsive EDL, the attractive van der Waals will dominate resulting in aggregation of the particles. For many systems it is expected that the surfaces remain in adhesive contact or coagulate in a primary minimum IF the only dominating forces were the DLVO forces. These ‘additional’ forces found in aqueous solutions have become known as ‘hydration forces’. Figure 1.6 shows experimental SFA data that show forces measured between mica surface in salt solutions of several concentrations. The force-distance curves show the characteristic repulsive DLVO force, and at short separations, the short-range repulsive force. The inset presents the data in more detail below 2 nm of separation where we observe the oscillatory hydration force.

Figure 1.6. DLVO and hydration forces between mica surfaces in monovalent electrolyte solutions. In dilute solutions the interaction is pure DLVO, characterized by an exponential repulsive force (double layer) and a short range attractive force (van der Waals). At higher salt concentrations, there appears a hydration force. The inset shows the hydration force in more detail below 2 nm in 1 M of KCl. Data adapted from Israelachvili, 1987.¹⁸

Historically, it was believed that water molecules form a solvation layer that acts as a repulsive barrier for an additional surface to approach.¹⁹ When the oscillatory hydration forces were first measured (shown in Figure 1.5), it was proposed that this structured layer of water molecules was the barrier and therefore the origin of the short-ranged repulsion. However, it became clear that this layered structure, and the resulting oscillatory force, was not detected in many systems where the monotonic repulsive hydration force was observed.²⁰ In soft, biological systems such as membranes for example, no oscillatory hydration forces were observed while the monotonic repulsive force was found.²¹ Even in rigid systems, such as glass-like silica surfaces, no oscillatory forces were found. It was believed that the roughness or the softness of the surface could ‘smear-out’ the layered arrangement of water molecules. But if there was no arrangement or layering, why was there still a repulsive barrier?

The magnitude of the repulsive monotonic hydration force was found to be affected by the type of ions present in solutions: the more hydrated

the ion, the more repulsive the interaction force.^{7, 22-25} Consequently, it was proposed that the repulsive hydration force was the result of the dehydration of adsorbed ions^{26, 27}, as was also believed to be the origin of the oscillatory hydration force. This is again contradicting, as it still does not explain why at some surfaces monotonic, but no oscillatory hydration forces were observed. In addition, repulsive short-range hydration forces were measured as well in purified water.²⁸ The latter indicates that the origin the hydration force cannot be the dehydration of adsorbed ions upon approaching surfaces. To complicate matters further, between two surfaces of different surface chemistry (silica vs mica in this example), this order (in magnitude of the force) was reversed – the more hydrated the ion present in solution, the lower the magnitude of the repulsive force.²⁰ This indicates that not only the solvent and the ions influence the hydration forces, the surface itself affects the force as well.

To gain insight into the origin of the monotonic hydration force, several theoretical models has been proposed. Attard and Batchelor suggested that the formation and rupture of hydrogen bonds between water molecules could result in repulsive forces at short distances.²⁹ The rupture of hydrogen bonds is an energetically unfavorable process and the decrease in the configuration number of the system diminished its entropy. Both of these effects contribute to the appearance of a repulsive force. According to Jönsson and Wennerström, the hydration force is simply the repulsive interaction between the surface dipoles (between phospholipid bilayers) and their respective induced polarization charges.³⁰ Marčelja and Radić proposed a mean-field theory to explain the short-range hydration force by the modification of water near surfaces by an order parameter that describes the local orientational structure of the liquid,³¹ that has an opposite sign at two identical surfaces, resulting in antisymmetric profiles. The forces associated with antisymmetric ordering is repulsive and decays exponentially. This means that if the order parameters profiles have the same sign, such that overlap of solvation layered leads to enhancement of ordering, the surface force is attractive. Therefore, in theory, it is predicated that the hydration force can be attractive.^{31, 32} Experimental studies have reported attractive short-range forces that were assigned to the hydration force.³³

The idea of orientated water is schematically shown in Figure 1.7. The arrows represent the orientation of a water molecule. Close to the surface, the water molecules form a layered regime, that results in the oscillatory hydration force (which is not taken into account in Marčelja and Radić's model). The regime that follows (termed cooperative ordering in this figure) is described in their model. Here, the water molecules are structured which is described with the order parameter. At the mid-plane, where the molecules of opposing surfaces meet, the water molecules are in opposite configurations that results in the repulsive forces.

Figure 1.7. Proposed idea of the orientations of water molecules at two opposing hydrophilic, charged surfaces leading to a layered regime (1) close to each surface, resulting in the oscillatory hydration force and to a monotonic hydration force (2) which is repulsive because the molecules are in opposite configuration to each other as they meet at the mid-plane. Data adapted from Israelachvili, 1987.¹⁸

There remains a gap between the proposed theoretical models and experimental observations, since (as described above) specific details in experiments affect the hydration force such as the surface and the specific ions in solution. Furthermore, until this day it remains unclear how and if the oscillatory and the monotonic hydration force are correlated. A lot of studies have been done^{34, 35}, and a lot of experimental data can be found in literature, but most of these either lack the resolution to detect the

oscillatory hydration force or report single observations based on innovative instrumental improvements.³⁶⁻³⁸ Impressive three-dimensional hydration maps show the layered interfacial structure at calcite^{37, 39} and mica surfaces³⁶. However, the monotonic contribution to the hydration force is largely ignored in these experiments. The (monotonic) hydration force has been measured between sharp probes (~ 1 nm radius tips) and mica surfaces in other experiments.^{28, 40} The monotonic contribution decays over 2 nm from the surface, which is longer than the decay of the modulation of the density of the water molecules.⁴¹ It is challenging to disentangle the DLVO interactions from the hydration force, since the length scales of these forces are very similar (specifically the van der Waals and the hydration force). In addition, there are no accepted theories that describe the interactions in the first few nanometers from the surface. The DLVO theory does not apply where the hydration force is found, since it is a continuum theory and we are trying to understand a discrete regime. It is believed that the hydration force is an ‘additional’ force next to DLVO interactions and it can be described by a monotonic and oscillatory decaying function.²⁸

1.5 Aim of this thesis

As discussed above, questions considering the (oscillatory) hydration force remain open till this day. Firstly, it remains unclear how and if the oscillatory and the monotonic hydration force are correlated: how do ions influence these ‘contributions’ to the force, and (how) are they affected by a different surface chemistry? To address these questions, one should measure the force and describe both contributions as a function of different types of ions, different salt concentration and measure the force at different types of substrates. Elevated temperatures are known to influence the magnitude of the solvation forces, whereby the layering remains stable.^{42, 43} The effect of temperature on the oscillatory hydration force is unknown.

In this thesis I present several studies where the hydration forces has been measured using Atomic Force Microscopy (AFM). In the discussion above I have shown data from older work where the SFA was used. The main difference between the two techniques is that one can use a very sharp probes to detect interacting forces in AFM experiments, while in

SFA, the liquid is confined between two large sheets. Furthermore, the AFM probe is driven with high precision such that small forces can be measured with great stability. More details about AFM will be given in Chapter 2. I choose to work (mainly) with mica surfaces since they are atomically smooth, easy to work with (upon cleavage they are clean) and due to the high intrinsic surface charge, water molecules orientate towards the surface.

At the start, I have addressed the questions on the influence of ions, and their specific hydration properties, by studying the effect of alkali ions (Li^+ , Na^+ , K^+ , Cs^+ , Rb^+) on the hydration force at mica surfaces. The aim is to study the effect of specific ions on the oscillatory and on the monotonic contribution to the hydration force. The work in this chapter (3) is supplemented by Molecular Dynamic simulations provided by colleagues from the Max Planck Institute of Biophysics, Frankfurt (Main), Germany. In the following chapter (4), I will describe the effect of divalent ions on the hydration force at mica surfaces. Specific divalent ions (Mg^{2+} , Ca^{2+} , Ba^{2+}) were studied and their influence on both the oscillatory and the monotonic contribution to the hydration forces are discussed. Following that, in chapter 5, the influence of the substrate was addressed by measured hydration forces at silica surfaces and, while using the same probe and solutions, the forces were measured at mica surfaces. Hereby, I investigate the influence of roughness (since silica is, unlike mica, not atomically smooth) and a different surface chemistry on the hydration force. Lastly, I present a study on mica surfaces in monovalent and in divalent containing salt solutions where the ambient temperature was varied.

1.6 References

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METHODS

2.1 Atomic force microscopy

Atomic force microscopy (AFM) has evolved into one of the most used techniques in nanotechnology. It is used in various research fields ranging from biology to physics. For academic purposes as well as in industry, AFM is most commonly used for topographical images. In contact mode, the simplest operation mode of AFM, the tip is brought in contact with the surface and then scanned laterally. The cantilever deflects due to interactions with the surface which is detected by the reflection of a laser beam from the cantilever. When the cantilever bends, the position of the laser spot on the photo-diode changes and is kept constant by adjusting the z piezo below the sample surface. The change in feedback, given in voltage, applied to the z piezo is the measured height signal and gives the topography of the surface.

In force distance mode, the topography is not of interest but the response of the cantilever is tracked while it is approached and retracted from the surface. The interaction forces between tip and sample can be extracted from the response of the cantilever. This can be done in dynamic and static mode. In static mode, the deflection of the cantilever is translated into a force F using $F = -k_c d$, where k_c is the spring constant of the cantilever and d the deflection. The probed force gradient should be smaller than the stiffness of the cantilever, otherwise the tip snaps in contact during approach. However, when using stiff cantilever, the sensitivity goes down because the deflection of the cantilever is smaller when measuring the same force. The sensitivity can be improved by using Dynamic force spectroscopy.¹

2.1.1 Dynamic AFM force spectroscopy

In dynamic AFM force spectroscopy one can measure the amplitude and phase or frequency shift with respect to the driving signal of the cantilever oscillation, in contrast to simply measuring the static deflection. The advantage of dynamic AFM is that the tip is not in contact with the surface and so during imaging, the applied forces on the sample are much smaller than in contact mode. The contact load is reduced and thereby the sensitivity increases considerably. In dynamic mode AFM, the cantilever is driven with an amplitude of typically 0.5 – 100 nm, which can be accomplished using several techniques (drive piezo, magnetic actuation or

photo-thermal excitation). In Amplitude Modulation AFM (AM-AFM), the drive frequency and the drive amplitude are kept constant, while the amplitude and phase response of the cantilever are monitored via a lock-in amplifier. The amplitude is compared to the set-point value and kept constant by adjusting the z -piezo. The feedback voltage from the z -piezo gives the height-signal, like in contact mode. In Frequency Modulation AFM (FM-AFM), the cantilever is subjected to a controlled feedback where it oscillates with constant amplitude, at the resonance frequency of one of the cantilever oscillation modes.² The advantage of AM-AFM over FM-AFM is that there is no feedback loop on phase or amplitude and thereby it is simpler and more robust, while in FM-AFM one can measure the conservative and dissipative forces in a decoupled manner.³ FM-AFM required two feedback-loop which makes its electronic complex and slow for operation in liquids, therefore it is often used in vacuum mostly used to obtain true atomic resolution images.^{4, 5}

Figure 2.1 Schematic of working principle of AFM where the cantilever is driven by the use of a blue laser. The cantilever is coated with gold/alumina and thermally bended by periodic laser exposure.

2.1.2. Amplitude modulation AFM

In this work, AM-AFM was used where the amplitude and phase response of the cantilever tip were probed, that is driven by photo-thermal excitation. The driving of the cantilever was done by locally heating it with a blue laser beam (Figure 2.1). The laser intensity I varies

harmonically as $I = I_0(1 + e^{j\omega t})$ where ω is the driving frequency and I_0 the amplitude of the oscillating intensity. The heating of the cantilever results in an oscillating temperature field over the cantilever, where the force and the tip deflection d is given by: $F = k_c(d - d_t)$, where d_t is the zero-load deflection due to the temperature enhancement along the beam caused by the laser radiation.

The amplitude and phase of the cantilever displacement are measured as a function of the tip-substrate distance to probe the influence of the interaction forces on the oscillation behavior of the cantilever. The measured response was analyzed by modeling the motion of the cantilever as a simple harmonic oscillator (SHO)^{4, 6-8}

$$m^*d^{**} + \gamma_c d^* + k_c d = k_c d_T(t) + F_{ts}(z + d, d) \quad (2.1)$$

where $m^*(k_c/\omega_0^2)$ is the mass of the cantilever, including the added mass due to the surrounding liquid, d is the displacement, ω_0 is the resonance frequency, $\gamma_c = k_c/(\omega_0 Q)$ is the damping coefficient, Q is the quality factor of the oscillator and F_{ts} the tip-sample interaction force. The amplitude of the tip oscillation was set smaller compared to the characteristic interaction length (< 0.5 nm) such that the interaction forces can be linearized as:

$$F_{ts}(z + d, d^*) = F_{ts}(z, 0) - k_{int}d - \gamma_{int}d^* \quad (2.2)$$

where $k_{int} = \partial F_{ts}/\partial z$ is the interaction stiffness (or force gradient), γ_{int} the interaction damping coefficient and $F_{ts}(z, 0)$ the equilibrium force at distance z . Solving the equation of motion of the harmonic oscillator (as can be found elsewhere⁶), the interaction stiffness and damping coefficient can be resolved:⁹

$$k_{int} = k_c \left[1 - \frac{\omega^2}{\omega_0^2} \right] \frac{A_\infty \cos(\varphi - \varphi_\infty) - A}{A} + \gamma_c \omega \frac{A_\infty \sin(\varphi - \varphi_\infty)}{A} \quad (2.3)$$

and

$$\gamma_{int} = \gamma_c \frac{A_\infty \cos(\varphi - \varphi_\infty) - A}{A} - k_c \left[1 - \frac{\omega^2}{\omega_0^2} \right] \frac{A_\infty \sin(\varphi - \varphi_\infty)}{\omega A} \quad (2.4)$$

where A and φ are the amplitude and phase of the cantilever deflection measured at a distance z from the substrate while A_∞ and φ_∞ are the amplitude and phase, measured at 140 nm from the substrate. To determine k_{int} and γ_{int} , the cantilever has to be calibrated to obtain the parameters k_c , γ_c and m^* . The stiffness is obtained from the thermal noise spectrum of the cantilever ($z > 1 \mu\text{m}$).¹⁰ The mass and the damping coefficient are obtained from the resonance frequency and the quality factor of the cantilever in liquid. Both are calibrated using the thermal noise spectrum measured at a distance of 140 nm from the surface where the tip-sample interactions are negligible. The resonance frequency and the quality factor are obtained by fitting the power spectral density of the SHO to the measured thermal spectral density. The force can be obtained by integrating k_{int} . However, in most of the figures presented in this work, we will show $k_{int} = -\partial F / \partial z$.

2.2 Experimental procedure

In this section I will describe the preparation procedures for the force spectroscopy measurements. When measuring hydration forces, it is crucial that all the used materials are clean: the surfaces of the instrument, as well as the substrate to be studied, the AFM probe, the tubing of the instrument and the solution in which the measurement will be performed.

Mica ($\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$) and silica substrates were used in this study. Mica is a group of phyllosilicate minerals that can easily be cleaved into thin pieces, giving a clean and flat surface of high intrinsic surface charge.¹¹ Because the surface is atomically flat, it is often used in SFA and AFM studies. Using small oscillation dynamic AFM, one can resolve the atomic lattice of the surface.¹² Silica on the other hand can be crystalline or amorphous. In our study, we use thermally grown amorphous silica surface. The Si-OH groups at the silica surface results in the characteristic hydrophilic nature.¹³

2.2.1 Preparation

Mica and silica substrates were glued using epoxy to a puck which is magnetically clamped to the piezo stage of the AFM (Asylum Research Cypher). The mica was cleaved with adhesive tape before each experiment. The thermally grown silica substrates were cleaned with ethanol and isopropanol, cleaned twice using an ultra-sonication bath for 20 minutes, after which the substrate was rinsed again with ethanol and isopropanol and lastly, placed in a plasma cleaner (PDC-32G-2, Harrick Plasma) for 20 minutes. The silica substrate was glued to the magnetic puck after the cleaning procedure, while the mica was cleaved after being glued to the puck. The tubing that is connected with the cell (used to insert the solvent) was rinsed with at least 20 mL of purified water (Millipore, resistivity 18.2 M Ω cm) to remove possible impurities. After this, the liquid cell of the AFM was cleaned with ethanol and isopropanol by rising it extensively. Each AFM experiment started by flushing the system with purified water. The electrolyte solutions were prepared by dissolving the salts (used salts are specified in the following chapters) in purified water. The pH is controlled and set to 3, 6 or 9 by either adding NaOH or HCl to the solution. All chemicals used were purchased from Sigma Aldrich and were used without further purification.

2.2.2. AFM probes

Ultra-high frequency cantilevers (ARROW-UHFAuD, nanoworld) with gold coating (detector side) and a very sharp tip were used. The length and width were 35 μ m and 42 μ m, respectively. The tip has an arrow shape and the force constant (k), resonant frequency (ω_0) and quality factor (Q) of the first eigenmode as determined in liquid were in the range: $k = 1.23 - 3.35$ N/m, $\omega_0 = 400 - 600$ kHz and $Q = 4 - 6$. These values have been determined in purified water and do not show significant variations in the salt solutions used in this study. The force constant was determined by using the thermal method. Prior to use, the cantilevers were cleaned by putting them in a bath of 1:1 ethanol/isopropanol for at least 15 minutes, after which they were dried using nitrogen and placed in a plasma cleaner for 20 minutes. The tips are composed of silicon but the outer layer of the probe is silica, which is the material that is in contact with the substrate (as will be discussed in subsection 2.4.1).

2.2.3. Force spectroscopy

Dynamic force spectroscopy measurements were performed using a commercial Asylum Research Cypher ES equipped with photo thermal excitation. The experiments were performed in liquid in a closed cell that allows exchange of liquid and control of the temperature (which was kept around 25 °C and was varied for the study presented in Chapter 6). The cantilever was immersed in a droplet of liquid (0.2 mL) that was sandwiched between the substrate and the top of the cell. Fluid was exchanged using glass syringes connected to the tubing. The drop volume was at least 25 times replaced by the new fluid and was left to equilibrate for 30 minutes before starting the measurements. During the measurement, the amplitude and phase of the cantilever deflection were tracked as function of z -piezo distance. For the measurement of the tip-sample interactions, the cantilever was driven at a fixed frequency ($\omega \approx 0.97 \omega_0$, where $\omega_0 \approx 450$ kHz) by an intensity-modulated blue laser diode that is focused on the gold coated topside of the cantilever close to its base. AFM measurements were operated with an oscillation amplitude of $A = 0.2 - 0.4$ nm. For each amplitude- and phase-distance curve, the cantilever was ramped over 5 nm. For each fluid composition, typically 200 approach curves were measured. A threshold value was used to limit the approach of tip and sample. This set-point was set such that a linear part in the deflection signal was observed due to the tip contacting the surface.

2.3 Data analysis

After the force inversion, the k_{int} curves were aligned, fitted and integrated to obtain the force-separation curves. As described in Chapter 1, most interaction forces between two bodies in liquid can be adequately described by DLVO theory (electrostatic interactions and van der Waals forces) up to the first few nanometers from the surface, where continuum theories do not apply anymore. In this study we focused on measuring interactions in the first 5 nm nanometers from the surface using very sharp AFM tips. In the following section I will describe the data analysis, the curve alignment and the subtraction of van der Waals interaction force (and why we did not take into account the electrostatic contribution to the force).

2.3.1 Force Alignment

After the conversion of the measured amplitude and phase signal into the k_{int} , all curves were aligned on the maximum of the first oscillation found in the force gradient, which was set at 0.12 nm. This sets the zero separation where we find the linear region in the deflection data indicating tip-sample contact. Figure 2.2. shows the raw AFM data: the phase, amplitude and deflection versus the drive voltage. The alignment was done on the force gradient, but this figure shows the signals used for the force conversion and the corresponding deflection: the phase and amplitude show oscillatory behavior due to the packing of the liquid near the surface, as was explained in Chapter 1.

Figure 2.2. Raw AFM data: phase, amplitude and deflection signal versus the piezo drive in V. After the force inversion, the force gradient is aligned on the maximum of the first oscillation which we set at 0.12 nm separation, as indicated here with the black line.

The straight line indicates the location of the maximum of the first oscillation. The dotted vertical line shows the 0 location, the wall, which matches with the 0 found in the deflection data indicated by the stripped horizontal line. Typically, more than 200 individual measured curves were

aligned for the plots presented throughout this thesis. Either all curves are shown or only the averaged curve. The averaged curve was calculated using data binning along the x axis with a binwidth of 0.02 nm. After aligning the curves, the averaged force gradients were fitted to obtain quantitative information of the data.

2.3.2 Fitting procedure

DLVO theory is an inadequate model of the non-continuum regime forces that were measured in this work at small separations, as was explained in Chapter 1. Therefore, we described the interaction force as a combination of structural (first term in equation (5)) and exponential decaying (second term) forces, which can be assigned to layering of the solvent and the decay of the monotonic forces:¹⁴

$$F = A_s \cos(2\pi\sigma z - \varphi) e^{\frac{-z}{\lambda_{osc}}} + A_m e^{\frac{-z}{\lambda_m}} \quad (2.5)$$

where A_{osc} and A_m are the magnitude of the oscillatory and the monotonic forces, φ is the phase shift, σ is the oscillatory hydration frequency, and λ_{osc} and λ_m are the decay lengths of the oscillatory and monotonic force. $\frac{1}{\sigma}$ corresponds to the size of the molecule that is packed near the substrate. Figure 2.3. shows experimental data and the fit and the two individual contributions.

Figure 2.3. Force gradient (N/m) versus apparent separation (nm) in 50 mM KCl. The experimental data is given in black open dots, the total fit in red, and the oscillatory term of the fit is given in blue while the exponential term is given in green.

The van der Waals force contributes to the monotonic part of the measured interaction force in our experiments. When trying to include the van der Waals force in the fitting procedure we observed significant variations, within the uncertainty (0 separation), in the magnitude of the monotonic contribution that varied from attractive to repulsive. Therefore, we choose not to include the van der Waals interaction in the fit. The electrostatic contribution to the force, as described in the DLVO theory, is not significant in our measurements. As explained in Chapter 1, the characteristic dimension of the diffuse layer thickness is known as the Debye length, which is affected by the concentration of ions. The ionic strength is $I_\infty = \frac{1}{2} \sum_i Z_i n_{i(\infty)}^2$, where i denotes each ionic species, $n_{i(\infty)}$ is the bulk concentration and Z_i the valency. The Debye length is given by:¹⁵

$$\lambda_D = \sqrt{\frac{\epsilon \epsilon_0 k_B T}{2 I_\infty e^2}} \quad (2.6)$$

In the following chapters, it is shown that the decay lengths of the interaction forces measured in this work do not scale with salt concentration (in a range from 0.01 – 4 M of salt), as the Debye length does. Therefore, we concluded that the measurement forces are not caused by continuum electrostatic interactions.

In this work we present the force gradient since that is the direct result of the force inversion that was used, therefore the data was fitted to the derivative of equation (5):

$$\begin{aligned} \frac{dF}{dz} = & \sqrt{(2\pi\sigma)^2 + \frac{1}{\lambda_{osc}^2}} A_{osc} \cos(2\pi\sigma z - \varphi - \text{atan}(2\pi\sigma\lambda_{osc})) e^{\frac{-z}{\lambda_{osc}}} \\ & + \frac{A_m}{\lambda_m} e^{\frac{-z}{\lambda_m}} \end{aligned} \quad (2.7)$$

An exponentially decaying weight function with a cutoff at 0.1 nm and a decay length of 1 nm was used in the fitting procedure. The cutoff is used to remove the short-range repulsive part of the data that corresponds to

direct contact with the substrate which is not of interest. The fitting procedure was done in MATLAB using the curve fitting tool, where the Trust-Region algorithm is used.

2.4 Van der Waals interaction

The van der Waals contribution to the force was not fitted as explained above, however, it does contribute to the total measured force. Therefore, we calculated the van der Waals interaction force between the used tip and the surfaces. Calculating the van der Waals contribution to the force comes with uncertainties, therefore, we performed an extended error analysis which is important if one wants to disentangle van der Waals from the total measured force with precision in the first few nanometers between interacting bodies. For two flat surfaces (per unit area), the van der Waals interaction force is defined as follows:¹⁵

$$F_{vdw} = -\frac{A}{6\pi z^3} \quad (2.8)$$

where z is the thickness of the medium (separation between tip and surface), A is the Hamaker constant. When calculating the interaction forces between the AFM tip and surface, the shape and radius of the tip needs to be described.

2.4.1. Tip shape

The importance of taking into account the exact geometry when calculating the van der Waals interaction has been pointed out in literature before.¹⁶ We have calculated the van der Waals force between a surface and a hyperbolic tip and between a surface and a sphere, both with a radius of 1 nm.

Figure 2.4: Force (nN) versus apparent separation (nm) measured at a mica substrate (1 mM BaCl₂). The calculated van der Waals interaction was subtracted from the force. The Derjaguin approximation was used ($R \gg z$) for the green and yellow curve. The red and green curves are the result of subtracting the van der Waals force calculated using a hyperbolic tip-plate geometry, while for the black and yellow curve, the sphere-plate geometry was used.

The calculated force was subtracted from a force that we have measured in experiments, the result is given in Figure 2.4. In addition, we have calculated the force with and without the Derjaguin approximation ($R \gg z$, where R is the tip radius in case of a spherical shape, and the semi-major axis in the hyperbolic case; z is the tip-sample separation). This analysis shows that this approximation works really well. However, we did choose to calculate the full volume integral since the geometric assumption of the Derjaguin approximation does not hold in our experiments (small tip size, see below). Since small forces are measured in the performed experiments, it is necessary to be able to calculate the van der Waals force as precise as possible. From the calculations given in Figure 2.4 we learned that the tip shape is important, mainly when the tip radius is larger than 1 nm (calculations not given in this figure). The exact tip shape and size of objects smaller than 5 nm cannot be resolved from SEM imaging, which is usually used for the imaging of AFM probes. Instead, we have used TEM to visualize used AFM tips, for which we had to cut off the probe

from the tip holder since the TEM sample holder is smaller than the AFM chip. This process was performed in a controlled environment with great precision (Supplementary Figures 2.2-2.6). The TEM image of a used AFM tip is given in Figure 2.5. The zoom-out TEM image is given in Figure 2.5B which shows a layer of ‘glue’ on one side of the probe that was attached during the process of preparing the TEM sample. During this process, the holder was cut from the tip after which the tip was glued to the TEM sample holder. The image given in part A was manually edited to remove the glue from the image. The semi-major axis is indicated by the thick white line between the end of the tip and the crossing of the dotted lines that follow the hyperbolic shape of the probe. The semi-major axis is 1.25 nm.

From the TEM images we have learned that the cross-section of the used tips is best described by a hyperbolic function. Therefore, we have calculated the van der Waals interaction using a volume integral between particle-particle interaction using a hyperbolic tip – plate configuration. We found the following equation which we used to calculate the van der Waals interaction force:

$$F(x) = \frac{A \tan^2 \frac{\theta}{2} (R z + z^2)}{5 z^3} \quad (2.9)$$

where A is the Hamaker constant, R and θ are the semi-major axis and the angle between the asymptotes of the hyperbolic cross-section of the tip respectively.

Figure 2.5: High resolution TEM image of a used AFM tip. The gray area around the tip is manually edited, the reason for this is clear from the B subfigure: Zoomed-out TEM image of the same probe, that shows a layer of glue (darker grey) on one side of the probe which is attached in the process of preparing the TEM sample.

The input parameter for the calculations presented in Figure 2.4 is the semi-major axis R . The x axis for the van der Waals calculations were shifted to the left such that the 0 separation distances was at -0.03 nm. This will be discussed in more detail in subsection 2.4.3. The crystalline Si structure of the tip is resolved, and from the ring around the Si core it is

clear that the outer shell of the probe is not a Si structure but rather the oxidized SiO_2 .

Figure 2.6: EF-TEM images of the base (a) and tip (b) of the AFM probe. The red signal represents the oxygen elements, while the green signal represents Si.

By the use of EF-TEM, we were able to visualize specific elements which we have used to check if an oxygen profile could be detected around the Si layer to verify the presence of a SiO_2 layer. Figure 2.6 shows the result, where red represents the oxygen signal and the green represents the signal from Si. It shows that oxygen and silicon signals are found around the edge of the probe, confirming the presence of SiO_2 .

The SiO_2 (silica) layer is at least 5 nm thick at the end of the tip, therefore we have used the dielectric constant and refractive index of silica when calculating the Hamaker constant.

2.4.2. The Hamaker constant

The Hamaker constant depends on the material properties of the interacting bodies and the intervening media. It can be approximated using the following equation:¹⁵

$$A = \frac{3}{4}kT \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right) \left(\frac{\epsilon_2 + \epsilon_3}{\epsilon_2 - \epsilon_3} \right) + \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 - n_3^2)^{\frac{1}{2}}(n_2^2 - n_3^2)^{\frac{1}{2}}\{(n_1^2 - n_3^2)^{\frac{1}{2}} + (n_2^2 - n_3^2)^{\frac{1}{2}}\}} \quad (2.10)$$

where (n) is the refractive index and (ϵ) the dielectric constant of the tip (1), the substrate (2) and the solvent (3). The dielectric constants and refractive indices that we have used are based on values found in literature, where we took into account that the forces are measured at an interface where these values are different from what is found bulk: the dielectric constant is lower¹⁷ due to the strong electric field of substrate and the refractive index is higher due to the higher concentration of ions near the substrate.¹⁸

Fluid properties such as refractive indices (n) and dielectric constants (ϵ) that were used are:

	n	ϵ
Mica	1.48	3.9
Silica	1.58	8.1
Solvent	1.371	10

We considered a dielectric constant of 10 for the solvent¹⁷ and a refractive index of 1.371 found for high salt concentration in water¹⁹. Furthermore, the dielectric constant and refractive index of the fluid change as a function of separation between the interfaces. We have analyzed how much this affects the calculation by calculating the force profile for two extreme Hamaker constants: using dielectric constants and refractive indices found in confinement and found in bulk. The reality as a function of separation will lie in between these values. The result is shown in Figure 2.7. The calculation shows that the influence on the curve is not significant, and therefore we conclude that this uncertainty of the Hamaker constant is not relevant in the calculation. In the following chapters we have used a Hamaker constant of $3.7e-21$, as found using values in

confinement (dielectric constant of 10 for the solvent¹⁷ and a refractive index of 1.371)¹⁹.

Figure 2.7. Force (nN) versus apparent separation (nm) measured at the mica substrate (1 mM BaCl₂). The calculated van der Waals interaction was subtracted from the data. Red line: Hamaker constant of $3.7e-21$. This constant was found using a dielectric constant and a refractive index as found in confinement^{17, 19}. Green line: Hamaker constant of $2.3e-21$, which was found using a dielectric constant and a refractive index as found in bulk.

2.4.3. Zero separation

The last uncertainty that we have considered in the calculation of the van der Waals force is the zero separation. The exact location of the surface cannot be determined in AFM spectroscopy since relative distances are measured from the z piezo displacements. By pressing the tip close to surface, it will become clear from the deflection signal if the tip contacts the surface from the linear part in the deflection curve (Figure 2.2). Therefore, it is possible to get a good approximation of the 0 separation from the deflection signal.

We did performed an error analysis where we chose various off-sets that shifts the x-axis and calculated the van der Waals force when using these differences off-sets. The resulting van der Waals force was

subtracted from a measured force. The result is given in Figure 2.8. It is more likely that the wall is on the left from the 0 location, therefore it is likely that the true off-set value is negative. Figure 2.8 shows that, in between realistic off-sets such as + and -0.03 nm, the force is not changing significantly. Only when shifting the x-axis with 0.1 nm to the right (which is not realistic), the calculated force affects the result significantly. We choose to calculate the van der Waals interaction using an off-set of -0.03 nm.

Figure 2.8. Force (nN) versus apparent separation (nm) measured at the mica substrate (1 mM BaCl₂). The calculated van der Waals interaction was subtracted from the data. The Hamaker constant ($3.7e-21$) and the tip shape (hyperbolic) were kept constant for all curves shown in this figure.

Hereby, we have shown the relevance of the uncertainties upon subtracting the calculated van der Waals interaction forces from measured forces in the first 5 nm from a surface. We learned that the Derjaguin approximation ($R \gg z$) is a good approximation but chose to calculate the full volume integral since the assumptions required are not fully met, owing to a small tip size. By imaging the used AFM probe by TEM, we were able to extract the exact details of the shape and tip and are therefore in a good position to calculate the van der Waals force contribution to the

measured forces. Uncertainties in the Hamaker constant and zero separation remain, however, we have learned that within the uncertainties, the resulting calculated force are not largely affected.

2.5 Concluding remarks

In the following chapters we have used the methods and analysis as described above. In Chapter 3 of this thesis, where we discuss the effects of alkali ions and pH on the hydration force at mica surfaces, we did not calculate the van der Waals force using the hyperbolic tip-shape, but rather used a sphere-plate geometry.¹⁵ SEM images show that the used tips have a radius that is smaller than the resolution of SEM can resolve. From the analysis and calculations based on the work presented in Chapter 3 we have learned the importance of the uncertainties in the tip shape and size when calculating the van der Waals force. Subsequently, we found a way to cut the AFM tip from the probe holder such that the tip could fit into the TEM sample holder, to obtain TEM images (of higher resolution). TEM images were obtained of the used AFM tips in the chapters 4, 5 and 6. In these chapters, the van der Waals calculation was done using the hyperbolic-tip shape as discussed above.

Specific details of the used salt solutions and substrates will be described in the methods sections in the following chapters.

2.6 Supplementary Information

Supplementary Figure 2.1. High resolution TEM image of a (different) used AFM tip. The semi-major axis is indicated by the white line between the end of the tip and the crossing of the stripped lines that follow the hyperbolic shape of the probe. The semi-major axis is 1.6 nm.

Supplementary Figures 2.2-2.6 (previous two pages). SEM images of the process of the TEM sample preparation of a AFM tip. The process was done using the Nova 600 Nanolab Dualbeam SEM/FIB, combining SEM and FIB (focused ion beam) etch and deposition. The tip was cut from the AFM tip holder. The ‘arm’ holds the tip after cutting, and allows to place it in the TEM sample holder.

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THE EFFECT OF ALKALI CATIONS AND PH

Hydration forces play a crucial role for a wide range of phenomena in physics, chemistry, and biology. Here we study the hydration of mica surfaces in contact with various alkali chloride solutions over a wide range of concentrations and pH values. Using Atomic Force Microscopy and Molecular Dynamics simulations, we demonstrate that hydration forces consist of a superposition of a monotonically decaying and an oscillatory part, each with a unique dependence on the specific type of cation. The monotonic hydration force gradually decreases in strength with decreasing bulk hydration energy leading to a transition from an overall repulsive (Li^+ , Na^+) to an attractive (Rb^+ , Cs^+) force. The oscillatory part, in contrast, displays a binary character, being hardly affected by the presence of strongly hydrated cations (Li^+ , Na^+), but becomes completely suppressed in presence of weakly hydrated cations (Rb^+ , Cs^+), in agreement with a less pronounced water structure in simulations. For both aspects K^+ play an intermediate role and decreasing pH follows the trend of increasing Rb^+ and Cs^+ concentration.

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Authors contributions: van Lin, S.R: performed AFM experiments, analysis of experimental data and contributed to writing the publication. Grotz, K. K. performed the MD simulations and analysis and wrote the

(method) sections on MD. Others contributed in writing the publication and discussions.

3.1 Introduction

Hydration forces are essential for the stability of many colloidal systems,¹ the assembly of soft biological and non-biological matter on molecular and supramolecular scales,²⁻⁴ the swelling of clays,⁵ wetting,^{6, 7} adhesion⁸ and lubrication,⁹ as well as the efficiency of catalysts.¹⁰ In all these cases, ‘reactants’ have to find each other under the influence of molecular interaction forces in the presence of an ambient solvent that frequently contains other solutes including in particular salts.¹¹ At separations of a few nanometers, these interaction forces and their salt-dependence are reasonably well described by the classical Derjaguin, Landau¹² Verwey, and -Overbeek¹³ (DLVO) theory of colloid science in combination with charge regulation equilibria.^{14, 15} ‘The last nanometer’ however, is generally governed by short range and hydration forces. On this scale, at the boundary between physics and chemistry the origin of the forces and their dependence on the water composition (salt content, specific ion effects, pH) are much more difficult to characterize and the contributions of different aspects such as surface hydration, bulk ion hydration and direct ion-substrate interaction are much more difficult to disentangle.¹⁶

In the present work, we focus on the effect of ions on hydration forces at atomically smooth mica-electrolyte interfaces, a well-characterized system that has been studied intensively since the pioneering works using the Surface Forces Apparatus (SFA) by Israelachvili and Pashley^{17, 18} in the 1980s. Recent advances in experimental techniques such as x-ray reflectometry and surface diffraction,¹⁹⁻²¹ non-linear optical spectroscopies,²² and Atomic Force Microscopy (AFM)²³⁻²⁵ along with powerful Molecular Dynamics (MD),^{26, 27} Monte Carlo (MC)²⁸ and Density Functional Theory (DFT)²⁹ simulations have produced detailed complementary insights into the structure and dynamics of interfacial water and casted doubt on some of the interpretations of earlier SFA experiments. However, a consistent picture has yet to emerge. For instance, hydration forces on mica have been reported to display either a monotonic exponential decay³⁰ as observed for silica^{31, 32} and many biological systems^{33, 34} or an oscillatory character.¹⁸ It has been argued that

hydration forces, in particular oscillatory ones, require the presence of ions.^{17, 18} Consequently, specific properties of the ions such as their hydration in bulk solution and/or ion-ion correlations would determine the characteristic spacing of force oscillations.^{25, 35-37} X-ray reflectivity and molecular simulations, however, typically report structural oscillations determined by the size of water molecules.^{20, 26, 27} Optical sum frequency generation measurements, on the other hand, report substantial orientational order of water molecules due to the alignment of water dipoles by local electric fields at polar surfaces.^{38, 39}

Compared to classical force-distance measurements with the SFA,^{18, 30, 35, 37} AFM^{23, 24} provides several advantages. In particular, it avoids confinement effects over a laterally extended contact area and thereby guarantees much better that ions and water molecules have sufficient time to equilibrate their configuration during the measurement. Moreover, much more local information can be extracted, yielding three-dimensional tip-sample force fields with atomic resolution and forces approaching the ones experienced by individual molecules, as suggested by the agreement between experiments and molecular simulations.⁴⁰⁻⁴⁴ However, the complexity and measurement time required to record such 3D force maps have so far hampered systematic AFM investigations for a substantial range of ionic species and concentrations, leaving at present a somewhat scattered picture of isolated observations.

In the present work, we harvest the speed and robustness of one-dimensional high-resolution AFM force mapping to provide the first comprehensive overview of hydration forces and structure at mica-water interfaces in presence of alkali chloride salts over a wide range of concentrations and pH values. Combining AFM spectroscopy and MD simulations, we demonstrate that the appearance of structured layers of water is indeed an intrinsic property of the pure system in the absence of any added salt. For all fluid compositions, the hydration forces can be described by a superposition of an oscillatory and a monotonically decaying part. Both respond in a different manner to the presence of salt and variation of pH. While periodicity and range are largely independent of salt concentration and pH, the monotonic repulsion disappears with increasing cation size. Most strikingly, the oscillatory part disappears for

weakly hydrated Rb^+ and Cs^+ ions beyond a certain threshold concentration. Molecular dynamics simulations demonstrate how the latter arises from the disruption of the intrinsic mica hydration layers by adsorbed bulky cations.

3.2 Methods

3.2.1 Experimental preparation

The mica substrate was glued using epoxy, to a steel puck which is magnetically clamped to the piezo stage of the AFM. The muscovite was cleaved with adhesive tape before each experiment. Each experiment started by flushing the system with purified water. The electrolyte solutions were prepared by dissolving the salts (NaCl , KCl , LiCl , RbCl and CsCl 99% purity) in purified water. The pH is controlled by either adding NaOH or HCl to the solution. The pH of the electrolyte solutions without adjustment is around 6. All chemicals used were purchased from Sigma Aldrich.

The experimental force curves were fitted to the following equation:

$$\frac{dF}{dz} = \sqrt{(2\pi\sigma)^2 + \frac{1}{\lambda_{osc}^2}} A_{osc} \cos(2\pi\sigma z - \varphi - \text{atan}(2\pi\sigma\lambda_{osc})) e^{\frac{-z}{\lambda_{osc}}} + \frac{A_m}{\lambda_m} e^{\frac{-z}{\lambda_m}} \quad (3.1)$$

where A_{osc} and A_m are the magnitude of the structural and the monotonic forces, φ is the phase shift, σ is the structural hydration frequency, and λ_{osc} and λ_m are the decay lengths of the structural and monotonic force. $\frac{1}{\sigma}$ corresponds to the size of the molecule that is packed near the substrate.

Information on the AFM experiments, data analysis and the fitting procedure can be found in Chapter 2. Information on the van der Waals calculation as well as an image of the used AFM tip (Supplementary Figure 3.16) can be found in the Supplementary Information of this chapter.

3.2.2 MD Simulations

We simulated muscovite mica $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ ⁴⁵ of dimensions 3.5 x 5 x 4.5 nm (5 layers with 48 unit cells each) using the CLAYFF force field⁴⁶ in simulation boxes of dimensions 3.5 x 5 x 11 nm, where the (001) plane was set to be orthogonal to the z axis of the simulation box. The exposed plane naturally contains potassium ions that were removed, the remaining mica crystal was hence negatively charged. We solvated the mica in TIP3P water.⁴⁷ We added 101 Li^+ , Na^+ , K^+ , or Cs^+ ions and for each system 5 Cl^- ions, to neutralize and to adjust to the experimental salt concentration of 50 mM LiCl, NaCl, KCl, or CsCl, respectively. We choose a recently developed ion force field that is designed to reproduce both thermodynamic and kinetic properties of aqueous solutions.⁴⁸ To mimic the measurements in pure water, protons were introduced (see Supplementary Information for details) to neutralize the system. Inserting the ions directly in the solution leads to a random adsorption of cations at the mica surface during the equilibration phase (Supplementary Figure 3.11).

MD Simulations were performed with GROMACS (version 5.1.3 and 2016.4).⁴⁹ Energy minimization was followed by two equilibration simulations (NVT and NPT) of 0.5 ns each. To constrain the bonds involving hydrogen to their equilibrium lengths, we employed P-LINCS⁵⁰ and used a time step of 2 fs. The temperature was kept at 300 K using the velocity rescaling thermostat of Bussi *et al.*⁵¹ and in case of the NPT equilibration the pressure was kept at 1 atm using the semi isotropic Berendsen barostat ($\tau_p = 5$ ps).⁵² Short-range van der Waals and electrostatic interactions were truncated at 1.2 nm. Long-range electrostatics were computed using the Particle Mesh Ewald method.⁵³ Following equilibration, all five simulations setups were run for 100 ns at constant pressure using a semi isotropic Parrinello-Rahman barostat ($\tau_p = 4$ ps).⁵⁴ The analysis of the simulation data was performed using MDAnalysis (version 0.15)⁵⁵ for Python. Trajectories were visualized using VMD (version 1.9.1).⁵⁶

We calculated the probability density of the water oxygen along the surface normal (z-axis). The first peak in the water density profile corresponds to a highly oriented first water layer. This first layer is

excluded from Boltzmann inversion to derive the potential of mean force (PMF) (see Supplementary Figure 3.12). The hydration force F is the first derivative of the PMF with respect to z and the force gradient is then the second derivative. To compare to experimental data, this force was normalized by an assumed sharp tip with radius of $R = 1$ nm, F/R .

To capture the orientation of water molecules in the vicinity of the mica surface, we describe the orientation of the dipole moment of water with the order parameter $\langle \cos \theta \rangle$, where θ is the angle between dipole vector and surface normal (see Supplementary Figure 3.14). As there was no AFM tip present in the MD simulations, the interaction between tip and mica was not part of the computationally derived hydration force and force gradient curves. The exponential term of the fit of the experimentally measured force curves (first term of equation (3.2)) was added to the computationally derived oscillatory hydration force curves for comparison.

3.3 Results and discussion

3.3.1 Dependence on specific ions

Hydration forces were measured using non-contact amplitude modulation AFM. 100-200 approach curves (grey lines in Figure 3.1a) were recorded for each fluid composition with the mica substrate and the AFM cantilever (SiO_2) fully immersed in the electrolyte solution (see Supplementary Information for details). The raw data were converted to forces using standard force inversion procedures.⁵⁷⁻⁶⁰ Subsequent averaging of the individual force gradient curves led to the final force gradient curves (thick green lines in Figure 3.1) and finally by numerical integration to force curves (thin black lines).

Figure 3.1. Averaged force gradient ($-dF/dz$; thick green lines) and normalized force (F/R thin black lines; $R=0.15$ (to fit both curves within the same y-axis)) versus apparent tip-sample separation measured in a pure water (light grey: 180 individual force curves). b-f various salts at a fixed concentration of 50 mM. All data were recorded with the same AFM tip at pH 6. Dotted lines: empirical fits to equation (3.1).

For pure water as well as the strongly hydrated Li^+ , Na^+ , and K^+ cations, the force gradient curves display a pronounced oscillatory character with up to three local maxima of the force gradient. The observation of oscillatory forces in de-ionized water (Figure 3.1a) demonstrates that force oscillations are an intrinsic property of pure confined water and does not require the presence of added salt, in contrast a widely accepted picture based on SFA measurements. The distance between adjacent maxima (or minima) varies between 0.28 and 0.35 nm and thus points to a pronounced layered arrangement of the water molecules within the first nanometer from the solid surface. In striking contrast, for Rb^+ and Cs^+ solutions, the AFM tip experiences a purely attractive force that increases monotonically from approximately 1 nm down to a 0.1 nm, where a strong repulsion sets in upon tip-sample contact. The oscillatory part of the force is completely suppressed.

Integrating the force gradient data reveals a second ion-specific aspect of the tip-sample interaction force: for the strongly hydrated cations the oscillatory force is superimposed onto a monotonically decaying repulsive background force. That monotonic force has a slightly larger range and can be detected up to distances of ≈ 1.5 nm. The strength of this force decays from Li^+ to Na^+ , almost vanishes for K^+ and changes sign to become attractive for Rb^+ and Cs^+ . Plotting the logarithm of the absolute value reveals that the force overall decays exponentially with increasing tip-sample distance. The same trends were recorded in several independent experiments with different samples and AFM tips (see Supplementary Figures 3.6 and 3.7).

The qualitative trends can be captured in quantitative numbers by fitting the force gradient data using an empirical function (dashed lines in Figure 3.1) consisting of a combination of a monotonically decaying exponential function $\phi_m(z)$ and a decaying oscillatory contribution $\phi_{osc}(z)$.^{11, 24}

$$\phi(z) = \phi_m^0 e^{-z/\lambda_m} + \phi_{osc}^0 \cos(2\pi z/d + \varphi) e^{-z/\lambda_{osc}} \quad (3.2)$$

A monotonic exponential decay is characteristic of hydration forces in many biological (membranes),^{33, 34} amorphous silica^{31, 32} and geological (clay swelling)⁵ systems. The additional oscillatory component is typical for rigid atomically smooth surfaces. Fitting to the experimental data reveals that the decay length of the oscillatory and the monotonic contribution are $\approx 0.2 \pm 0.08$ nm and 0.4 ± 0.1 nm and do not display any appreciable dependence on the type of cation. The disappearance of the oscillatory force and the appearance of an attractive monotonic force for Rb^+ and Cs^+ are reflected in the vanishing values of ϕ_{osc}^0 and the reversal of the sign of ϕ_m^0 (see Supplementary Figure 3.1).

3.3.2 Concentration dependence

A possible explanation of the monotonically decaying force are electrostatic interactions between two effectively charged surfaces interacting across an electrolyte solution, as recently suggested.⁶¹ The effective surface charge on mica and silica (AFM tip) results from the negative bare surface charge that is partially compensated by specific

adsorption of cations. For weakly adsorbing cations, the effective surface charge on both surfaces is expected to be negative leading to repulsion in solutions of LiCl and NaCl. On the other hand, more strongly adsorbing cations, such as Rb^+ and Cs^+ , could reverse the surface charge of mica or the AFM tip leading to attraction between the two surfaces with opposite effective charge.^{62, 63} If the behavior of the monotonically decaying force was indeed caused by continuum electrostatics in combination with charge regulation, its range would be determined by the Debye screening length λ_D and thus vary with the salt concentration. To falsify this assumption, we repeated the measurements for selected salts of variable concentration (Figure 3.2). While the details vary slightly, the overall behavior for Li^+ and K^+ is essentially the same for all concentrations.

Figure 3.2. Averaged ($n = 50$) force gradient ($-dF/dz$; thick lines) and normalized force (F/R thin black lines) versus apparent tip-sample separation for LiCl a, KCl b, and CsCl c for several concentrations as indicated. Each salt was measured with a separate AFM tip at pH 6. Dashed lines: empirical fits to equation (3.1).

All curves display the same oscillatory solvation structure superimposed onto an ion-specific but largely concentration-independent monotonic background. In particular, the spacing between local maxima and minima is consistent with the diameter of water up to the highest concentration investigated. In contrast, for Cs^+ the force oscillations disappear around a critical concentration of 1 mM. For all concentrations above that threshold, the force becomes purely attractive as already seen in Figure 3.1.

In the critical concentration range of about 1 mM, Cs^+ -containing solutions display a bistable behavior. Consecutively recorded force curves alternate between the characteristic water-like response with an oscillatory

structure and the purely attractive behavior, which is unique for Cs^+ and Rb^+ at high concentrations. Typically, each of the two types of response is observed for several consecutive approaches before the system switches to the other. For this specific concentration, it thus seems that there are two configurations in which the system can get trapped for extended periods of time (4 - 5 sec). Qualitatively, this observation is consistent with the long residence times of ≈ 100 ms of Rb^+ ions on mica that were reported in recent AFM measurements⁶⁴ and with the slow ion exchange rates in x-ray-based $\text{Na}^+ - \text{Rb}^+$ ion exchange reactions.¹⁹ According to the AFM studies⁶⁵ and recent x-ray measurements⁶⁶, the mica surface is only partially covered by cations for approximately mM concentrations. The steepness of the adsorption isotherm in this concentration range in combination with lateral attractions promotes the formation of patches of adsorbed ions.⁶⁵ Such patches would be expected to display very slow collective dynamics that could explain our observations.

Figure 3.3. Averaged ($n = 50$) force gradient ($-dF/dz$; thick lines) and normalized force (F/R thin black lines) versus apparent tip-sample separation measured at selected bulk pH values. Dashed line: empirical fit. The pH was adjusted by either adding HCl or NaOH.

3.3.3 pH dependence

Early SFA studies of hydration forces reported that the presence and strength of hydration forces requires the presence of ions beyond a certain threshold concentration of up to 10 mM.^{17, 18} Moreover, the strength of the hydration forces is thought to correlate with the bulk hydration energy of the cations.¹⁷ Our observations clearly show that for sharp AFM tips the oscillatory part of the hydration forces can also be observed in the absence of any added salt (Figure 3.1a). This is consistent with the oscillatory density profiles extracted from x-ray reflectivity measurements^{19, 20} as well as MD simulations^{26, 27} and supports the idea that the oscillatory part of the hydration forces experienced by an AFM tip indeed originate from the density of the interfacial water.⁴¹⁻⁴³ In the absence of added salt, hydronium ions are likely to compensate the intrinsic negative surface

charge of mica, as has been suggested by other studies^{17, 66}. Interestingly, hydronium ions turn out to have a similarly destructive effect on the oscillatory hydration structure of the interfacial water as the bulky Rb^+ and Cs^+ ions: The amplitude of the oscillatory force component decreases with decreasing pH and a slightly attractive monotonic contribution develops (Figure 3.3). While the suppression is less pronounced than in case of Cs^+ ions, the first signs of a reduction can already be detected in pH 2.5, *i.e.* at a similar H_3O^+ cation concentration as for Cs^+ .

These observations have several direct implications. First, whenever the forces display an oscillatory component, the spacing between subsequent local force maxima is always close to the diameter of a water molecule, independent of salt concentration and pH. Neither our experiments nor our simulations (see below) display any indication of wider separations due to the potential formation of ion pairs or due to the expulsion of completely hydrated cations.^{25, 35, 37} We believe that the smallness of the tip-sample contact in AFM experiments with sharp tips (as compared to SFA and colloidal probe AFM) is essential for observing this intrinsic behavior of the mica-electrolyte interface, which is consistent with the structure of the electric double layers reported in x-ray measurements^{19, 20} and MD simulations.^{26, 27} Second, because the range of the forces in Figure 3.2 remains limited to ≈ 1 nm while the Debye screening length varies by a factor of ≈ 30 , the origin of the monotonic force cannot be attributed to electrostatic screening. Instead, we can rationalize the invariance of the decay length in terms of the phenomenological model by Marcellia and Radic.⁶⁷ According to this mean field model, an exponentially decaying long range force arises from the polarization of water molecules that are induced at the solid-liquid interface. The decay occurs on a length scale that is governed by the correlation length of the water. The observed invariance of the decay length upon adding salt indeed confirms that the decay is governed by the intrinsic properties of water, largely independent of the added ions. In contrast, the strength of the hydration force is imposed by the degree of order and polarization imposed on the water and thus directly by the microscopic electric fields and hydrogen bonding between the first layer of water and the substrate – including adsorbed ions. Depending on their

specific size, adsorption site, and configuration (e.g. inner shell vs. outer shell), adsorbing ions affect the intrinsic hydration structure of the mica surface in an ion specific manner.³³

Third, the salt-dependence of the monotonic part of the force cannot be attributed to van der Waals interaction. While definitely contributing to the total force, van der Waals interaction cannot explain the change in sign of the monotonic part of the force upon changing the salt species and concentration. For the present system, the van der Waals force is always attractive with a Hamaker constant (based on bulk properties) that varies between -8.4×10^{-21} J (pure water) and -5.1×10^{-21} J (4 M KCl). Hence, we conclude that the ion-specific response of both the oscillatory and the monotonic part of the tip-sample interaction are dominated by the microscopic hydration structure of the mica-electrolyte interface.

3.3.4 MD simulations

To analyze the ion specific structure of interfacial water in more detail, we performed MD simulations for aqueous alkali chloride concentrations (50 mM) as in Figure 3.1 (see Methods and Supplementary Information for details). Cations were found to adsorb to the mica surface to compensate the intrinsic negative surface charge. The preferred adsorption sites were found to shift with increasing ion size from the oxygen triad above an Al atom for Li^+ towards the center of the ditrigonal cavity for Cs^+ (Figure 3.4 and Supplementary Figures 3.10 and 3.11), in agreement with previous MD simulations.^{26, 27, 68} Similarly, the corresponding electron density profiles normal to the surface displayed a reasonable agreement with earlier x-ray reflectivity and surface diffraction.^{20, 66} Cations were found to exchange with the bulk at rates that decrease according to $\text{Na}^+ > \text{K}^+ > \text{Cs}^+ > \text{Li}^+$, implying that the forces experienced by the AFM tip on typical measurement time scales (several ms) represent thermally averaged configurations of both interfacial water and adsorbed ions.

The interfacial water structure is characterized by two quantities, the density profile and the water dipole orientation order parameter $\langle \cos \theta \rangle$. In the first water layer in direct contact with the mica surface, water molecules are highly oriented with both hydrogen atoms pointing towards the negatively charged oxygen atoms of the mica crystal (Figure 3.4b). The order parameter $\langle \cos \theta \rangle$ indicates that the water dipoles are

more strongly oriented for Cs^+ compared to Li^+ (Figure 3.4e). This results from the fact that small, strongly hydrated cations perturb the substrate-induced orientation of the first water layer more strongly than larger ones. Beyond the first layer, we observe two additional pronounced maxima in the water density for all ions except Cs^+ . Despite this pronounced positional order, water molecules in the second and third layer display a much weaker preferential orientation (Figure 3.4e), as also reported elsewhere.⁶⁹ In addition to decreasing orientational order, the maxima in the water density are much less pronounced and broader for Cs^+ (Figure 3.4c). Thus, adsorbed Cs^+ ions disrupt both the orientational and the positional order of interfacial water beyond the first water layer.

To compare the simulation results to the AFM data, we calculated the unit cell-averaged potential of mean force experienced by water molecules as a function of distance from the surface following the procedure proposed by Watkins and Reischl that has been applied successfully for several systems.^{41-43, 61} The resulting force and force gradients obtained by differentiating the potential of mean force display oscillations that reflect the oscillations of the water density (Figure 3.4c,d and Supplementary Figure 3.13). The force oscillations thus indeed arise from the layered water structure of the interfacial water. Consistent with the experimental observations, the simulations show that this layered water structure is only weakly disturbed by strongly hydrated cations (Li^+ , K^+ , and also by Na^+ see Supplementary Figure 3.13). In contrast, the bulky Cs^+ ions, which disturb the water layering substantially suppress the force oscillations. The local reduction of the water density in the vicinity of the Cs^+ ions, which is also observed in the bulk⁷⁰ is crucial for this effect. This leads to shorter residence times of water in the vicinity of Cs^+ compared to other cations and consequently to weaker hydration forces.²⁷

Figure 3.4. Water structure at the mica/water interface for LiCl (left), KCl (middle), and CsCl (right). *a* Adsorbed ions and oriented water molecules in the first layer. *b* Side view displaying strong water layering in the presence of Li⁺ and K⁺ and the disruption of layering for Cs⁺. *c* Normalized force (black) and water density profile (red) from MD simulations. *d* Force gradient from MD (green), experimental force gradient curves (gray) after subtraction of monotonic contribution (dashed). *e* Order parameter for orientation of water, defined as $\langle \cos \theta \rangle$, where θ is the angle between dipole moment of water and surface normal (see Supplementary Figure 3.14).

The force gradient based on the numerical calculations agrees almost quantitatively with the oscillatory part of the experimentally measured data (Figure 3.4d). The simulations reproduce in particular the remarkable robustness of the force oscillations against the presence of small hydrated cations as well as their disappearance in the presence of Cs^+ . Note that the comparison excludes the region of the first water layer, where the molecules are tightly squeezed in between the adsorbed cations. Most likely, these ions are not displaced by the AFM tip during the experiments. In contrast to the oscillations, the monotonic contribution of the hydration forces is not captured by the simulations. As we will discuss below, detecting this contribution seems to require a ‘macroscopic’ object as a probe, such as the AFM tip. Our observation agree with x-ray diffraction studies, where it was found as well that the interfacial hydration layers are less ordered in the CsCl solutions compared to solutions containing K^- , Na^- , or LiCl .²⁰

To interpret these results, we consider the work $\Delta W = \Delta W_m + \Delta W_{osc}$ performed upon approaching the AFM tip to the sample.

Figure 3.5. Mechanical work upon approaching tip and sample in units of kJ/mol (left axis) and equivalent number of H-bonds (right axis) vs. Gibbs free energy of cation hydration in bulk⁷¹. Data taken from Figure 3.1. a Red circles are the total work of the monotonic part of the force. Blue filled squares correspond to total work corrected using van der Waals interaction with macroscopic Hamaker constants; open blue squares are the best estimate for total hydration work based on adjusted Hamaker constant. See text for details. b Total work of the oscillatory part of the force and equivalent number of H-bonds (right axis).

For the monotonic contribution of the force, we find values of $\Delta W_m = \int \int \phi_m(z') dz' dz \approx -2.8 \dots + 6.4 kT$ for bringing the tip from a distance of 1.5 nm to 0.2 nm (red circles in Figure 3.5a). These values contain contributions from both monotonic hydration forces and direct tip-sample forces due to van der Waals interaction. The latter needs to be subtracted in order to extract the contribution due to hydration. If we use the bulk values of the refractive index and the dielectric constant to calculate the Hamaker constants A for the various electrolytes, we obtain positive values of $\Delta W_m^{hydr} = \Delta W_m + \frac{AR}{6D}$ for all salts and concentrations investigated (filled blue squares in Figure 3.5a and Supplementary Figure 3.2-3.5).

However, estimating the direct tip-sample interaction based on bulk fluid properties provides an overestimation of van der Waals interactions because the dielectric constant decreases close to the substrate⁷² due to hindered rotation of the water molecules and the refractive index increases (in particular for the heavier cations) due to the enhanced local ion concentration. Correcting for the reduced Hamaker constant (see Supplementary Information for details) results in a best estimate for ΔW_m^{hydr} , which is positive for all salts, implying repulsive hydration forces (open blue squares in Figure 3.5a and Supplementary Figure 3.2-3.5). With the exception of H_3O^+ , the strength of the hydration force is found to decrease with increasing ion radius, largely following the order of the bulk hydration energy (Figure 3.5a).

It is also important to appreciate the smallness of the absolute value of ΔW_m^{hydr} of only a few kT. Using the tip geometry and the bulk density of water ($\rho_{H_2O} = 33 \text{ nm}^{-3}$) we estimate that this amount of work is distributed over ≈ 1000 water molecules that are transferred from the interfacial region between tip and sample to the ambient bulk. In the final state, these molecules are engaged in ≈ 2000 H-bonds (avoiding double counting). Given the strength of a H-bond of $\approx 3 \text{ kT}$ (without separating the molecules),⁷³ we conclude that the changes in the water structure correspond to the equivalent of breaking only a few H-bonds. Taking the thickness of the interfacial water layer to be 1 nm, one-in-thousands H-

bonds corresponds to an excess interfacial energy of $\approx 0.4 \text{ mJ/m}^2$. Compared to the bulk cohesive energy and the total mica-electrolyte interfacial energy, the average perturbation per water molecule due to hydration effects is thus rather weak.^{74, 75} Presumably, this also explains why the monotonic contribution of the force is not resolved in our (and other) MD simulations based on the potential of mean force approach for a single water molecule. These forces are only resolved in measurements and simulations that explicitly include a ‘macroscopic’ object such as an AFM tip, which integrates the forces due to a large number of water molecules. A similar argument has been discussed in the context of hydration pressures in biological systems.¹⁶

Performing the same analysis for the oscillatory part of the hydration forces yields a somewhat different picture. Integration over several oscillations leads to minor values for $\Delta W_{osc} = \int \int \phi_{osc}(z') dz' dz$ because of cancellation effects between regions with attractive and repulsive forces. Yet, even upon displacing the tip, say, from first minimum in the force gradient at a separation of $\approx 0.3 \text{ nm}$ to the first maximum at $\approx 0.15 \text{ nm}$ also ΔW_{osc} amounts only to a fraction of kT (Figure 3.5b), *i.e.* substantially less than the binding energy of a single H-bond. Therefore, we conclude that the work involved in the tip displacement must be absorbed by a slight distortion of the dynamically reorganizing H-bonding network amongst the water molecules involved in the process. Their number, however, is more difficult to estimate than above because it depends strongly on the details of the tip geometry. MD simulations of atomically resolved AFM images with explicit tips suggest that only very few water molecules are involved⁴²; geometric estimates provide an upper limit of a few tens of molecules.

The dependence on the ionic species (and thus the bulk hydration energy) of ΔW_{osc} is very different from the monotonic hydration force. Given the locality of the interactions it is in fact quite plausible that the details of the local binding environment provided by the surface and the adsorbed cations control the ion specificity of ΔW_{osc} rather than the bulk hydration energy. This is consistent with the numerically calculated water density profiles.

3.4 Conclusion

In summary, our work shows that the hydration forces at smooth mica-electrolyte interfaces are composed of two contributions, an oscillatory one that is determined by the direct interactions between solid, ions and water on the scale of one to two molecular layers and a monotonically decaying one that ranges up to three or four water layers. While the overall strength of the hydration interactions amounts to the equivalent of breaking only a few H-bonds, the dependence on the cation species decreases by up to a factor of 4 between strongly hydrated Li^+ ions and weakly hydrated Rb^+ and Cs^+ ions. The latter two cations completely disrupt the oscillatory force profiles that are characteristic for the mica-water interface, while the profile remains stable in the presence of the more strongly hydrated alkali ions. These findings shed light on the relative importance of different aspects of solvation and hydration for chemical reactions involving small molecules (*e.g.* in catalytic processes¹⁰) as compared to contact formation, adhesion, friction, *etc.* on the colloidal scale.

3.5 Supplementary information

3.5.1 Van der Waals interaction and Hamaker constant

The van der Waals interaction and Hamaker constant were calculated using the following equations:

$$W_{vdw} = \frac{-AR}{6d} \quad (S3.1)$$

$$A = \frac{3}{4}kT \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right) \left(\frac{\epsilon_2 + \epsilon_3}{\epsilon_2 - \epsilon_3} \right) + \frac{3h\nu_e}{8\sqrt{2}} \frac{(n_1^2 - n_3^2)(n_2^2 - n_3^2)}{(n_1^2 - n_3^2)^{\frac{1}{2}}(n_2^2 - n_3^2)^{\frac{1}{2}}\{(n_1^2 - n_3^2)^{\frac{1}{2}} + (n_2^2 - n_3^2)^{\frac{1}{2}}\}} \quad (S3.2)$$

where a tip radius (R) of 5 nm was used and a cutoff distance (d) of 0.2 nm, to remove the short-range repulsive part of the data that corresponds to direct contact with the substrate. Bulk fluid properties such as refractive indices (n) and dielectric constants (ϵ) that were used are considered as an upper limit of the Hamaker constant. n is extrapolated from the approximately linear salt concentration / n dependence. The lower limit of the Hamaker constant was calculated using ϵ as found in confinement and n as calculated for high salt concentrations (> 4 M). The used values and references can be found in Supplementary Table 3.I.

3.5.2 MD Simulation in pure water

After removing all potassium cations from the exposed planes of mica, the crystal carries a negative charge. In order to assure charge neutrality in the simulation box containing solely pure water and no compensating cations, we developed the following description to neutralize the system without disturbing interactions. Initial energy minimization and NVT equilibration were performed using force field parameters as for potassium⁷⁶ adjusting only the mass to match that of a hydrogen atom. During NPT equilibration we reduced the ϵ -value of the Lennard-Jones potential in three steps to

nearly zero (0.001 kJ/mol). Comparison of the resulting water density along the surface normal to x-ray reflectivity measurements⁷⁷ validated our approach to be reasonably close to experiment (Supplementary Figure 3.9).

3.5.3 Atomistic model for mica

The exposed sheets of muscovite mica $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ ⁷⁸ contain a silicon (Si, grey) to aluminum (Al, pink) ratio of 3:1. It is generally not known where exactly the Al and Si atoms are located within the crystal. In the CLAYFF force field,⁷⁹ charge delocalization is captured by usage of multiple parameters for similar atoms, i.e., bridging oxygen atoms next to tetrahedral coordinated aluminum atoms (in purple in Supplementary Figure 3.10) carry a slightly more negative partial charge than those bridging silicon atoms (red). In this work, the Al atoms are oriented in straight lines leading to two kinds of hexagonal ring cavities, as has been done before.⁶⁵ One containing a single Al atom (purple) and two more negative partially charged oxygens (purple) and the second cavity containing two Al (pink) and four slightly more negative oxygen atoms (purple).

3.5.4 Preferred binding sites

Supplementary Figure 3.11 shows the preferred binding sites for the cations at the surface of mica from our simulations. Depending on their size, the cations occupy different binding sites. H^+ and Li^+ preferentially bind to the two slightly more negative oxygen atoms next to aluminum. Na^+ and K^+ have two distinct binding sites. They can bind either to the two oxygen atoms next to aluminum (similar to H^+ and Li^+) or form contacts with all six oxygen atoms of a ditrigonal cavity (similar to Cs^+). Cs^+ preferentially binds to the ditrigonal cavity. By contrast, the exchange of the cations with bulk does not depend on their size or charge density. Exchanges are observed most frequently by Na^+ ions and the frequency of exchanges decreases according to $\text{Na}^+ > \text{K}^+ > \text{Cs}^+ > \text{Li}^+$.

3.5.5 Potential of mean force

The probability density of the oxygen atoms of the water in the interfacial region was calculated along the surface normal (Figure 3.4c and Supplementary Figure 3.13c) with a resolution of 0.02 nm, comparable to

the resolution in AFM measurements. The first peak of the water density could not be resolved in experiments and was therefore excluded for the calculation of the hydration forces. Hence the water density starting after the first peak was used for Boltzmann inversion to calculate the potential of mean force (PMF) along the surface normal (green dots in Supplementary Figure 3.12). Continuous splines (blue in Supplementary Figure 3.12) were fitted through these discrete data points. Subsequently the first (hydration force) and second derivative (gradient of the hydration force) were taken.

3.5.6 Results from MD simulations for pure water and NaCl

Supplementary Figure 3.13 shows the results from our MD simulations for pure water and the NaCl solution, similar to Figure 3.4 in the main text. Water molecules in the first layer with direct contact to the mica surface are highly oriented (Supplementary Figure 3.13a,e). For both pure water and in the NaCl solution, we observe two additional pronounced maxima (Supplementary Figure 3.13b,c). Similar to Figure 3.4, the force gradient based on numerical calculations agrees almost quantitatively with the oscillatory part of the experimentally measured data (Supplementary Figure 3.13d). The simulations reproduce in particular the remarkable robustness of the force oscillations against the presence of small hydrated cations.

3.5.7 Supplementary figures and tables

Supplementary Figure 3.1. Fit coefficients indicating the strength and decay length of a the monotonic and b the oscillatory contribution to the hydration force (data from Figure 3.1). The left axis of figure a indicates the magnitude and the right axis shows the decay length of the monotonic part of the hydration force. The left axis of b shows the amplitude of the first oscillation in N/m and the right axis shows the decay length of the structural part of the force.

Supplementary Figure 3.2. Mechanical work upon approaching the tip towards the substrate in units of kT/molecule versus concentration of LiCl. Data taken from Figure 3.2. *a* Monotonic force integrated from 1.5 to 0.2 nm. Filled red circles: total work; blue squares: total work corrected using van der Waals interaction with macroscopic Hamaker constant; blue open squares: best estimate for total hydration work based on adjusted Hamaker constant. *b* Oscillatory force ϕ_{osc} from 0.3 nm to 0.15 nm. Left axis shows the work in kT/molecule, the right axis shows the number of hydrogen bonds.

Supplementary Figure 3.3. Mechanical work upon approaching the tip towards the substrate in units of kT/molecule versus concentration of KCl. Data taken from Figure 3.2. *a* Monotonic force integrated from 1.5 to 0.2 nm. Filled red circles: total work; blue squares: total work corrected using van der Waals interaction with macroscopic Hamaker constant; blue open squares: best estimate for total hydration work based on adjusted Hamaker constant. *b* Oscillatory force ϕ_{osc} from 0.3 nm to 0.15 nm. Left axis shows the work in kT/molecule, the right axis shows the number of hydrogen bonds.

Supplementary Figure 3.4. Mechanical work upon approaching the tip towards the substrate in units of $kT/\text{molecule}$ versus concentration of CsCl. Data taken from Figure 3.2. Monotonic force integrated from 1.5 to 0.2 nm. Filled red circles: total work; blue squares: total work corrected using van der Waals interaction with macroscopic Hamaker constant; blue open squares: best estimate for total hydration work based on adjusted Hamaker constant.

Supplementary Figure 3.5. Mechanical work upon approaching the tip towards the substrate in units of kT/molecule versus bulk pH value. Data taken from Figure 3.3. *a* Monotonic force integrated from 1.5 to 0.2 nm. Filled red circles: total work; blue squares: total work corrected using van der Waals interaction with macroscopic Hamaker constant; blue open squares: best estimate for total hydration work based on adjusted Hamaker constant. *b* Oscillatory force ϕ_{osc} from 0.3 nm to 0.15 nm. Left axis shows the work in kT/molecule, the right axis shows the number of hydrogen bonds.

Supplementary Figure 3.6. Force gradient profiles versus apparent separation in 50 mM of a LiCl, b KCl and c CsCl averaged over $n = 50$ individual curves. The grey dotted lines are set on the maxima of the oscillation as found when measuring the force gradient in pure water, to indicate possible shifts in location of maxima upon measuring in these salt solutions.

Supplementary Figure 3.7. Force gradient profiles versus apparent separation in 50 mM of a LiCl, b KCl and c CsCl averaged over $n = 50$ individual curves, as measured using a different tip and different mica substrate compared to Supplementary Figure 3.6. The grey dotted lines are set on the maxima of the oscillation as found when measuring the force gradient in pure water, to indicate possible shifts in location of maxima upon measuring in these salt solutions.

Supplementary Figure 3.8. Force gradient profiles versus apparent separation in different concentrations of NaCl, averaged over $n = 50$ individual curves. The grey dotted lines are set on the maxima of the oscillation as found when measuring the force gradient in pure water, to indicate possible shifts in location of maxima upon measuring in these salt solutions.

Supplementary Figure 3.9. Water density along mica surface normal measured from x-ray reflectometry (red) and from MD (black).⁸⁰

- tetrahedral silicon, st, charge: 2.1000 e
- tetrahedral aluminum, at, charge: 1.5750 e
- bridging oxygen, ob, charge: -1.0500 e
- bridging oxygen with tetrahedral substitution, obts, charge: -1.1688 e

Supplementary Figure 3.10. Model surface of mica used in MD simulation. Aluminum atoms (pink) are aligned in straight lines. Purple bridging oxygen with tetrahedral substitution atoms are slightly more negatively charged than those bridging silicon (red).

Supplementary Figure 3.11. Binding sites of cations at the mica surface for pure water, LiCl, NaCl, KCl, and CsCl, respectively. Binding along lateral rows is due to composition of the crystal, as oxygen atoms next to aluminum carry a slightly more negative charge.

Supplementary Figure 3.12. Potential of mean force (PMF) derived from Boltzmann inversion of the density of water oxygens along the surface normal (green dots). The first peak of the water density was excluded. Continuous splines were fitted (blue).

Supplementary Figure 3.13. Water structure at the mica/water interface for pure water (left) and NaCl (right). a Adsorbed ions and oriented water molecules in the first layer. b Side view displaying strong water layering. c Normalized force (black) and water density profile (red) from MD simulations. d Force gradient from MD (green), experimental force gradient curves (gray) after subtraction of monotonic contribution. e Order parameter for orientation of water, defined as $\langle \cos \theta \rangle$, where θ is the angle between dipole moment of water and surface normal.

Supplementary Figure 3.14: Water molecule and its dipole moment as used in this study. The orientational order parameter $\langle \cos \theta \rangle$ (Figure 3.4e, Supplementary Figure 3.13e) is defined over the angle between this dipole vector and the surface normal.

Supplementary Figure 3.15: Mica imaged by the use of AFM in purified water.

3

Supplementary Figure 3.16: SEM images of a used AFM probe to measure the interaction forces, where a radius of 5 nm is found. This probe has been pressed into hard contact for calibration after the force measurements.

Supplementary Table 3.I. Refractive indices and dielectric constants used to calculate the van der Waals contribution.^{72, 81-83}

	concentration (M)	ϵ	n
LiCl	0,005	74,4	1,333
	0,01	72,8	1,333
	0,05	80	1,334
	0,5	68	1,338
KCl	0,005	74,4	1,333
	0,05	80	1,333
	2	60	1,352
	4	50	1,371
CsCl	0,0003	79,2	1,333
	0,001	76,8	1,333
	0,01	72,8	1,333
	0,05	77,8	1,334
RbCl	0,05	80	1,334
NaCl	0,05	80	1,333
mica		8,1	1,55
silica		3,81	1,44
confinement	0,05	10	1,371

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THE EFFECT OF DIVALENT CATIONS

The influence of hydration forces adjacent to interfaces is crucial to understand the interactions of materials in aqueous environments. The importance and questions related to the hydration force have been pointed out in fields ranging from biology, chemistry to physics. In this chapter, we present our investigation on the effect of divalent ions on the oscillatory hydration forces at mica-electrolyte interfaces. We show that the intrinsic water layering at mica surfaces remains stable in the presence of different types of divalent ions up to 1 M, in contrast to what was found for different alkali ions. While the oscillatory hydration force is mostly unaffected, the monotonic part of the hydration force is attractive at intermediate divalent ion concentrations, but becomes slightly repulsive at concentrations of 1 M. Furthermore, we show that the magnitude and sign of the hydration force is not only affected by the type of ion present, but also by the substrate.

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4.1 Introduction

Hydration forces are at play between well-solvated surfaces in water and balances the van der Waals attraction in the first nanometer from the substrate. The hydration force exhibits an exponential decay with a decay length of 1-2 nm.¹ Next to the exponentially decaying short-range force, an oscillatory contribution to the hydration force was found that decays into the bulk.² The existence and relevance of the hydration force is found in systems as diverse as organic molecule adsorption,³ DNA precipitation,⁴ to friction/lubrication⁵. For instance, it is shown that the formation of a strong hydration layer provides efficient boundary lubrication, and can therefore be used to lubricate materials.^{6, 7} The hydration force is studied extensively for decades, yet, it's origin and dependence on surfaces and fluid composition is still controversial from experimental and theoretical point of view.⁸

To gain insight into the origin of the monotonic hydration force, several theoretical models have been proposed. Attard and Batchelor suggested that the formation and rupture of hydrogen bonds between water molecules could result in repulsive forces at short distances.⁹ The rupture of hydrogen bonds is an energetically unfavorable process and the decrease in the configuration number of the system diminished its entropy. Both of these effects contribute to the appearance of a repulsive force. According to Jönsson and Wennerström, the hydration force is simply the repulsive interaction between the surface dipoles (between phospholipid bilayers) and their respective induced polarization charges.¹⁰ Marčelja and Radić proposed a mean-field theory to explain the short-range hydration force, in which the local structure of the water near surfaces was described by an order parameter,¹¹ that has opposite values at two identical surfaces, resulting in antisymmetric profiles. The forces associated with antisymmetric ordering is repulsive and decays exponentially. This means that if the order parameters profiles have the same sign, such that overlap of solvation layered leads to enhancement of ordering, the surface force is attractive. Therefore, in theory, it is predicated that the hydration force can be attractive.^{11, 12}

The hydration force has been measured intensively since the pioneering works by Israelachvili and Pashley, who revealed using the

Surface Force Apparatus (SFA), the short-ranged hydration force between mica sheets in the presence of a critical bulk concentration of alkali ions.¹³ ¹⁴ Later, many more reports followed where the repulsive hydration forces was studied in monovalent salts.¹⁵⁻¹⁹ However, very limited studies focus on the effect of divalent salt solutions on hydration forces, likely due to the fact that it is reported in the 1980s that there was no hydration force found below 1 M of divalent cation solutions, which was explained by a lack of divalent ion adsorption at lower salt concentrations.^{20, 21} However, recently it was shown by x-ray reflectivity measurements²² that divalent ions do adsorb on mica surfaces below 1 M. Furthermore, as shown in the previous chapters, the hydration forces are present between mica and silica tips even in the absence of added salts.²³ In addition, oscillatory hydration forces are reported in the presence of 150 mM of MgCl_2 at the mica-electrolyte interface.¹⁹ The latter studies use the advances of sub-nanometer oscillation amplitude Atomic Force Microscopy (AFM), while using sharp probes. Hereby the nature of the (oscillatory) hydration force can be studied in detail. However, it remains unclear how divalent ions of different hydration energies affect the hydration force. In addition, it is unclear why the repulsive hydration force was measured in alkali solutions in the older SFA experiments, while it was not reported in divalent containing salt solutions of similar concentrations.

Recently, we have reported a systematic study of the hydration force at the mica-alkali interface, where we show oscillatory hydration forces measured by AFM using sharp probes.²³ From this study we have learned that the oscillatory force is stable in the presence of small alkali ions, such as Li^+ , Na^+ and K^+ but that it is suppressed in the presence of the more bulky ions, such as Cs^+ and Rb^+ .²³ In the present study, we follow up on that work by firstly studying the hydration force at mica surfaces in the presence of different types of divalent ions (Mg^{2+} , Ca^{2+} and Ba^{2+}). Hereby we look into the two contributions to the hydration force: the monotonic and oscillatory part. Secondly, we study the influence of the substrate on the hydration force by comparing forces measured at mica and silica substrates. Lastly, we looked into the effect of the presence of mono- and divalent ions on the hydration force at mica substrates. As pointed out above, the effect of Cs^+ ions on the oscillatory hydration force is clearly

visible since it suppresses the oscillatory contribution. Here, we are interested in the effects of Cs^+ ions on the hydration force in the presence of Ba^{2+} ions at the mica-electrolyte interface.

This chapter is organized as follows: first, we discuss the oscillatory contribution to the hydration force, where we show the effect of divalent ions and the combination of mono- and divalent ions on the hydration force at the mica substrate. In the following section we discuss the monotonic contribution to the hydration force, which we discuss by presenting the numerical integral of the force gradient. In the final part we discuss the implications of our findings.

4.2 Methods

4.2.1 Experimental preparation

Mica and silica substrates were glued using epoxy to a puck which is magnetically clamped to the piezo stage of the AFM. The mica was cleaved with adhesive tape before each experiment. The silica substrates (thickness of $\text{SiO}_2 > \sim 30$ nm) were cleaned with ethanol and isopropanol, cleaned twice using an ultra-sonication bath for 20 minutes, after which the substrate was rinsed again with ethanol and isopropanol and lastly placed in a plasma cleaner for 15 minutes. The silica substrate was glued to the magnetic puck after the cleaning procedure, while the mica was cleaved after being glued to the puck. Each AFM experiment started by flushing the system with purified water. The electrolyte solutions were prepared by dissolving the salts (CsCl , MgCl_2 , CaCl_2 , BaCl_2 (98% purity)) in purified water. The pH of 50 mM of divalent salt solutions is around 5, which was adjusted to 6 by adding NaOH . All chemicals used were purchased from Sigma Aldrich.

The experimental force curves were fitted to the following equation:

$$\frac{dF}{dz} = \sqrt{(2\pi\sigma)^2 + \frac{1}{\lambda_{osc}^2}} A_{osc} \cos(2\pi\sigma z - \varphi - \text{atan}(2\pi\sigma\lambda_{osc})) e^{\frac{-z}{\lambda_{osc}}} + \frac{A_m}{\lambda_m} e^{\frac{-z}{\lambda_m}} \quad (4.1)$$

where A_{osc} and A_m are the magnitude of the structural and the monotonic forces, φ is the phase shift, σ is the structural hydration frequency, and λ_{osc} and λ_m are the decay lengths of the structural and monotonic force. $\frac{1}{\sigma}$ corresponds to the size of the molecule that is packed near the substrate. More information on the fitting procedure, AFM experiments, data analysis and the van der Waals calculations can be found in Chapter 2.

4.3 Results and discussion

4.3.1 Oscillatory hydration forces in the presence of divalent cations

Hydration forces at the mica-electrolyte interface were measured using non-contact amplitude modulation AFM. Figure 4.1 shows the force gradients measured in several divalent containing salt solutions.

Figure 4.1. Force gradient ($-dF/dz$ (N/m)) versus apparent separation (nm) measured in 1, 10, 100 and 1000 mM of $MgCl_2$, $CaCl_2$ and $BaCl_2$ at a mica substrate. The thin gray lines are individual measured curves, the thick, black line is the averaged of these lines and the red, dotted line is the fit to equation (4.1).

Several ($n > 200$) individual curves are shown in gray lines. Subsequent averaging of the individual force gradient curves led to the thicker black lines, the red dotted line is the fit (equation 4.1). The force gradient measured in 1, 10, 100 and 1000 mM of MgCl_2 , CaCl_2 and BaCl_2 is shown in column 1, 2 and 3 respectively. The data presented in this figure was obtained using the same AFM probe. All the force gradient curves display an oscillatory character. The distance between adjacent maxima (or minima) is ~ 0.25 nm and thus points to a pronounced layered arrangement of water molecules within the first nanometer from the mica surface.²⁴ Our previous work in combination with MD calculations (presented in Chapter X) and others studies^{23, 25, 26} point out that the oscillatory contribution to the hydration force is the result of the modulation of the density of water at the mica-water interface. As was presented in Chapter 3, the forces measured at the mica-water interface display pronounced oscillatory behavior, that remains stable in the presence of the smaller alkali ions, such as Li^+ , Na^+ and K^+ , while the oscillatory contribution to the force was completely suppressed in the presence of the bulkier Rb^+ and Cs^+ ions. Here we show that the oscillatory hydration force is stable in divalent ion containing salt solutions, independent of the size of the divalent ions. The size of the hydrated divalent cations used in this study varies between 0.318 (for Mg^{2+}) to 0.326 nm (for Ba^{2+}).²⁷ The separation between the maxima in the oscillatory force is ~ 0.25 , therefore we conclude that we do not probe the exclusion of hydrated cations or the formation of ion pairs but rather the removal of water molecules.¹⁹ We believe that we probe the intrinsic properties of the mica-electrolyte interface due to the use of sharp AFM tips. Our observations are consistent with x-ray measurements at the mica-electrolyte interface and MD simulations where similar structural profiles with a periodicity of 0.25 were found at the mica-electrolyte interface.^{28, 29} An interesting observation of the force gradient presented in Figure 4.1 is that the force gradient is attractive in most of the conditions, while the oscillatory contribution to the force is stable. This is different from what we found when studying the effect of monovalent ions on the hydration force, where we found a monotonically decaying attractive force in the presence of Cs^+ and Rb^+ ions, and repulsive, oscillatory hydration forces in the presence of smaller alkali ions.

Furthermore, the periodicity of the oscillatory force is not significantly different when changing the salt solutions, but the amplitudes of the first oscillation are influenced by the salt concentration and ion type. The amplitude of the first oscillation was quantified by fitting the experimental data to an empirical function consisting of a combination of a monotonically decaying exponential function and a decaying oscillatory contribution, as is described in equation (4.1). Figure 4.2 shows the fit parameters of the oscillatory contribution to the data presented in Figure 4.1: the amplitude (N/m) of the first oscillation and the decay length, λ_{osc} (nm).

Figure 4.2. Fit parameters of the oscillatory part of the force: amplitude (N/m) and decay length (nm) as a function of concentration (mM). All parameters presented here were extracted from the data presented in figure 4.1.

The amplitude of the oscillations found in the force gradient is an indication for the stability of the water layers: the higher the amplitude, the more stable the layers since more energy is required to penetrate through them. The highest amplitude is found in purified water (Supplementary Figure 4.1). The addition of divalent ion salt solutions does affect the amplitudes but there is no clear trend as a function of

concentration or salt type. At 10 mM, the lowest amplitude was found for all divalent salt solutions studied here. The presence of the divalent cations lowers the stability but does not completely suppress the water layering, not even at 1 M of salt. The decay length of the structural hydration force is ≈ 0.2 nm, independent of salt concentration or salt type.

4.3.2 The oscillatory hydration force in the presence of mono- and divalent cations

In the experiment presented in Figure 4.1, we have looked into ideal conditions, where only one salt type is studied, to avoid the inability to distinguish the effect of ions. However, in most environments, such as seawater for example, many different ionic species are present. It is proposed in literature that organic molecules are released from binding to a surface by the exchange of divalent ions, which bridge polar organic molecules, with monovalent cations.³⁰ As was suggested by this study, the hydration of both ions and surface play an important role in adsorption processes at mica surfaces. Here, we show hydration forces measured at the mica-electrolyte interface in the presence of different ratios of CsCl and BaCl₂ solutions (the total molarity is not kept constant).

Figure 4.3. Force gradient ($-dF/dz$ (N/m)) versus apparent separation (nm) measured in different ratios of CsCl:BaCl₂ solutions given in mM: 0:50, 1:50, 10:50, 20:50, 50:50, 50:20, 50:10, 50:1 and 50:0. The thin differently colored lines are individual measured curves, the thick, black line is the averaged curve and the red, dotted line is the fit to equation (4.1).

The data is shown in Figure 4.3, where the thin colored lines are individual measurements, and the thick black line is the average of all these curves. The red, dotted line is the fit to equation (4.1). The oscillatory hydration force is measured in all conditions except for the ratios 50:10, 50:1 and 50:0 CsCl:BaCl₂ (mM).

We have shown in our previous work, that the oscillatory hydration force is suppressed in the presence of CsCl solutions, where the presence of 3 mM of CsCl already affects the amplitude of the oscillatory force.²³ In combination with MD simulations we have shown that the water density near the surface is significantly lower in the presence of Cs⁺, resulting in the lack of a pronounced oscillatory force profile at the mica-electrolyte interface.²³ The data presented in Figure 4.3 shows that the

presence of CsCl (50 mM) does not suppress the oscillatory force as long as there are sufficient Ba^{2+} ions present. In the current experiments, the hydration force is influenced by both Cs^+ and Ba^{2+} , and the oscillatory profiles show that the presence of Ba^{2+} out-competes the effect of Cs^+ , up to the point where there is more Cs^+ compared to Ba^{2+} . Figure 4.4 shows the fit parameters of the oscillatory contribution to the data presented in Figure 4.3: the amplitude (N/m) of the first oscillation and λ_{osc} (nm). Figure 4.4 shows that the amplitude increases upon increasing the amount of BaCl_2 (mM) in solution. In the presence of 50:0, 50:1 and 50:10 mM of CsCl: BaCl_2 , no oscillatory hydration force was measurement, which is represented in the figure with an amplitude of 0. In the conditions 20:50, 10:50, 1:50 and 0:50, when there is more BaCl_2 compared to CsCl, the amplitude of the oscillation increases, up to the point where the highest amplitude is found in solutions containing only BaCl_2 . Recently it was reported, by XRD, that Cs^+ ions adsorb in higher amounts on mica surfaces compared to Ca^{2+} ions when both CaCl_2 and CsCl salts are present in solution.³¹ From which it was concluded that the hydration forces are more important than electrostatics since from charge point of few, the divalent ions would adsorb more strongly. The authors show that both cations adsorb inside the cavity of the mica lattice and must therefore lose a significant part of their hydration shell which is easier for Cs^+ ions compared to Ca^{2+} . A recent MD study³² has shown that divalent ions have a stronger adsorption strength compared to monovalent ions due to higher charges, however, but they did find lesser adsorption of divalent cations compared to monovalent ions (as was found by the XRD study). It was proposed that the high hydration energy of the divalent ions results in an effective larger size of the ion, which leads to lesser absorption and earlier saturation.³² Both of these studies show that divalent ions adsorb in lesser amounts on mica surfaces compared to Cs^+ ions, but that the hydration energy of the divalent ions is higher compared to the monovalent ion.

Figure 4.4. Amplitude (N/m) and λ_{osc} (nm) extracted from the data presented in Figure 4.3.

Force spectroscopy data does not provide information on the concentration of adsorb cations, and therefore we cannot directly compare these findings. However, we do learn that there is a need of more Cs^+ ions, compared to Ba^{2+} ions to induce the suppressing effect on the oscillatory force. From MD studies we know that the adsorption energy is higher of divalent ions compared to monovalent ions, which also means that it requires more energy to remove the divalent ions compared to monovalent ions. Here we show that when there are 5 times more Cs^+ ions compared the Ba^{2+} ions, the characteristic oscillatory-suppressing effect of Cs^+ ions are observed in the force gradient.

The forces presented in Figure 4.3 are attractive in all conditions studied, which is not surprising since we have shown in Figure 4.1 and in our previous work (presented in Chapter 3), that in the presence of Ba^{2+} and in the presence of Cs^+ ions, the short-range force is attractive. Adding both ions to the solution results in an attractive force as well.

4.3.3 The short-range force in the presence of divalent cations

To study the effect of the salt concentration and cation type on the interacting force, the gradient as presented in Figure 4.1 was numerically integrated to obtain the force. The result is presented in Figure 4.5, where Figures 4.5A, B and C show the forces measured in MgCl_2 , CaCl_2 and BaCl_2 respectively. The forces measured in MgCl_2 and CaCl_2 show a similar trend as a function of concentration, where the largest attractive force is found at 100 mM of salt and a repulsive force is found at 1 M. In addition, the magnitude of the force is dependent on the type of divalent cation present: the magnitude of the force measured in 10 mM of CaCl_2 is by a factor of ~ 3 larger compared to the force measured in 10 mM of BaCl_2 .

It is known from x-ray studies that divalent ions of different sizes (such as Mg^{2+} , Ca^{2+} and Ba^{2+}) differ in adsorption heights at mica surfaces, which directly influence the water density at the mica-electrolyte interface.²² Similarly, MD simulations show that Ca^{2+} ions adsorb closer to the surface compared to Mg^{2+} . This difference is explained by the fact that Mg^{2+} ions retain their hydration shell upon adsorption, while Ca^{2+} retain only part of its hydration shell. [not published?] These studies point out that the interfacial layer is different in the presence of ions of different sizes or hydration energies. Here we show that the difference in adsorption height of Ca^{2+} and Mg^{2+} , as shown by MD, results in hydration forces that differ in magnitude: in the presence of Ca^{2+} , the magnitude of the attractive force is larger compared to the magnitude of the force found in the presence of Mg^{2+} . How the adsorption height of the ion directly influences the force is not obvious but it can be argued that the water orientation is affected by the ions: whether its hydration shell is intact or partly disrupted upon adsorption can influence the orientation of the polar solvent.

Figure 4.5. Force (nN) versus apparent separation (nm) measured at the mica-electrolyte interface at 1, 10, 100 and 1000 mM of MgCl₂ (A), CaCl₂ (B) and BaCl₂ (C). This is the result of numerical integration of the force gradient curves as presented in Figure 4.1.

To make this point stronger, we looked into the decay lengths of the interacting forces. If the behavior of the forces was indeed caused by continuum electrostatics, its range would be determined by the Debye

screening length and thus vary with the salt concentration. As can be observed in Figure 4.5, the decay lengths of the forces measured in 1 mM up to 1 M have a very similar decay length. For this reason, we also do not calculate or try to fit the electrostatic forces since the data shows that the forces that we measure are not the result of the continuum electrostatic forces described by DLVO, as was also shown with the experimental data presented in Chapter 3.

The experimental data presented in Figures 4.1 and 4.5 was reproduced, using a different tip (of the same type) and a different mica sheet, where similar trends are observed. This data is presented in Supplementary Figures 4-7. The forces measured in these experiments are, in most cases, very small, and thereby, the differences found in different salt solutions or concentrations are also small. Therefore, we cannot expect that the trends are exactly the same in two different experiments. However, we did reproduce the attractive forces at the mica substrate in the presence of divalent ions below 1 M, and found again repulsive forces at 1 M, for all salt types studied here. To interpret the results presented in Figure 4.5, we calculated the work, $W(kT)$, by integrating the area of the force curve, which is the work done by the AFM probe to get to the mica substrate. The calculated work is plotted in Figure 4.6 in blue symbols (total work) for the three different salt solutions as a function of concentration.

The work is found to be negative for all divalent cations at 1, 10 and 100 mM of salt, and positive at 1 M. The $W(kT)$ in the presence of divalent ions is smaller compared to what we find in the presence of alkali ions, as presented in Chapter 3. We discussed, based on the work found in the presence of alkali ions, that we only break a handful of hydrogen bonds in the gap between the AFM tip and the mica substrate. Here we show that even less energy is required to break up the hydrogen bonded network in the presence of divalent ions, which points out that the hydrogen bonded network is less stable (compared to monovalent cations) once divalent ions adsorb on mica surfaces. The force in the first nanometers from the substrate is influenced by the van der Waals interaction, so in order to look only into the contribution of the hydration force, we calculated the van der Waals interaction and subtracted its energy from the work values, the

result is presented in red symbols in Figure 4.6. Details of the calculation of the van der Waals interaction can be found in Chapter 2.4.

Figure 4.6. Mechanical work upon approaching tip and sample in units of kT versus concentration of salt (mM): the result of the integral of the force presented in Figure 4.5. The blue symbols are the result of this integral from 5 nm to 0.1 nm. The red symbols correspond to the work after subtracting the van der Waals contribution.

Interestingly, the work values found in 1, 10 and 100 mM of CaCl_2 and 1 mM BaCl_2 are negative after subtracting the van der Waals contribution, which indicates that the interacting force is attractive after subtracting the van der Waals interaction.

The work values are the result of the integral of the forces curves presented in Figure 4.5, from 5 nm to 0.1 nm from the surface. The reason for this cut-off of 0.1 nm is clear from Figure 4.7. Close to the surface, the interaction force is repulsive due to hard-wall contact which will result in negative values of the total work. However, the exact cut-off position will influence the absolute value for the work significantly. For example, the ‘hydration’ work shown in Figure 4.6 in red symbols is positive for 100 BaCl_2 indicating a repulsive interaction force. However, if we look at the hydration force given in Figure 4.7 (the force after subtracting the

calculated van der Waals force) the overall interaction force as a function of separation is attractive at this salt concentration. The work values give you an impression of the energy needed to approach the surface, however, to discuss the total interaction force, one needs to consider the force profile as function of separation, as given in Figure 4.7.

Figure 4.7. Force (nN) versus apparent separation (nm) measured at the mica-electrolyte interface at 1, 10, 100 and 1000 mM of MgCl_2 (A), CaCl_2 (B) and BaCl_2 (C). This is the result of the subtraction of the calculated van der Waals interactions from the forces presented in Figure 4.5.

The van der Waals force is very small in the presented experiments due to the use of very sharp tips (1.25 nm, see Chapter 2). Therefore, the forces remain to be attractive over 5 nm separation after subtracting the

calculated van der Waals interaction (except for the forces measured in 1 M). As discussed above, the largest magnitude of the force is found in Ca^{2+} solutions.

The data shows that, after subtracting the van der Waals interaction, the short-range force between hydrophilic surfaces can be attractive. However, it is important to realize and analyze the relevance of the uncertainties when subtracting the van der Waals interaction from the total force in the first few nanometers from the surface. We performed an extended error analysis which is crucial if one wants to disentangle the hydration force from the van der Waals interaction. This analysis and discussion can be found in Chapter 2.4.

4.3.4 The attractive short-range force

The short-range hydration forces that we report show a pronounced oscillatory behavior due to the modulation of water molecules at the mica substrate which is an interface-induced effect, superimposed onto an attractive monotonic background. Most studies report a repulsive hydration force between hydrophilic surfaces,^{5, 16, 33-35} though there are reports that provide evidence for attractive water-mediated short-range forces.^{36, 37} The origin of the hydration force is debated,^{12, 38} but the most accepted hypothesis attributes the force to the energy required to remove the orientated water molecules from the surface, because of strong hydrogen bonding interactions. In the 1980s, SFA experiments reported a lack of a repulsive hydration force in divalent containing salt solutions below several molars of salt.²⁰ In their previous reports the same authors showed repulsive hydration forces between mica surfaces in the presence of monovalent salts,¹³ which was attributed to the repulsion of the hydrated ions adsorbed on the mica surfaces. The question is: why do they measure repulsive hydration forces in alkali ions between mica sheets (below 1 M) and not in divalent ion solutions? They explained it by the fact that divalent ions do not adsorb on the mica surfaces, due to competition with hydronium ions. However, as mentioned in the introduction of this chapter, we know from x-ray diffraction measurements that divalent ions are present at the mica surface in salt solutions below 1 M.³⁹ In addition, we have shown that oscillatory hydration forces can be measured in the absence of salt solutions.²³

Our experimental data, acquired using sharp AFM tips, shows indeed that there is no repulsive hydration force in the presence of divalent cations at mica surfaces, but an attractive force due to the combination of the hydration force and the van der Waals interaction. In addition, the oscillatory contribution to the hydration force at the mica-divalent cation interface is resolved in our measurements, which was not reported in the older SFA experiments. Due to charge screening by ion adsorption, the SFA measurements are dominated by van der Waals interactions, which results in the collapse of the mica-mica sheets. Due to the stiffness and sharpness of the AFM probes, the tip does not snap into contact by the van der Waals interaction but rather follows the layering of water at the substrate. At high salt concentrations (>3 M), Pashley et al. did observe a repulsive force. We observed a small repulsive force as well at 1 M of salt, but show that the interaction force at low and intermediate concentrations of divalent containing salts is attractive. We do point out that we cannot directly compare our experimental forces with those acquired in SFA experiments since the forces measured in this AFM study were measured using sharp, silica-based probes while in SFA experiments, forces are measured between mica sheets. Thereby, the geometry and the surface chemistry are different. However, from our experiments we learn that, in the presence of divalent ions, the short-range interaction force can be attractive, where the magnitude of the force depends on the type of divalent ion and its concentration.

As was mentioned in the introduction, Marčelja and Radić proposed a theory that can explain an attractive water-mediated short-range force between surfaces by an order parameter that describes the orientation of water molecules.¹¹ If the order parameter profiles have the same sign, the overlap of the hydration layers leads to enhancement of ordering, such that the force is attractive. The order parameter is the same in a symmetric system: where the surface chemistry of the interacting substrates is the same. To understand the influence of the substrate on the monotonic contribution to the hydration force, we have measured hydration forces at both mica and silica surfaces in pure water and in 50 mM of CaCl_2 , using the same tip. In the experiments using a silica AFM tip and a silica surface, we create a symmetric system in terms of surface chemistry, while in the

experiments using a mica surface and a silica AFM tip (see Chapter 2), we measure forces in an asymmetric system.

4.3.5 The influence of the substrate

In Figure 4.8 we present the data measured at the mica- and silica-interface while using the same AFM tip. Figure 4.8A shows the force gradient as a function of separation measured at the mica and silica substrate in purified water and in 50 mM of CaCl_2 . Integration of this curve led to the curves presented in Figure 4.8B. In Figure 4.8C we show the force from which we have subtracted the van der Waals interaction, for which we have used a Hamaker constant based on a mica-silica and silica-silica system (see Chapter 2 for the details). The data shows that the force (gradient) is repulsive at the mica- and silica-water interface, both showing an oscillatory character. The oscillatory character is more pronounced in the force gradient (Figure 4.8A). Due to numeral integration of the gradient to the force, the oscillations are less pronounced. The existence of the oscillatory hydration force at silica surfaces is highly debated in literature¹⁵, since it has been predicated theoretically but it has never been measured (to our knowledge) in force spectroscopy. Our data clearly shows that the force gradient has an oscillatory character at the silica-electrolyte interface, where the amplitude of the first oscillation is very comparable to what is found at the mica-water interface. Interestingly, the second maxima of the hydration layer at the mica substrate is found at $x=0.54$ while the second maxima at the silica substrate is found at $x=0.40$. This could indicate that the packing of water molecules, resulting in the oscillatory force profile, is not just simply the interface-induced layering as observed for large molecules such as OMCTS.⁴⁰ The hydrogen bonded network, influenced by the charge of the surface, is likely to play an important role in stabilizing the water molecules in the interfacial layer.

From the forces, presented in Figure 4.8B, it is clear that the force is more repulsive at the mica-water interface compared to the silica-water interface. As was discussed based on the data presented in Figure 4.1 and 4.5, in the presence of CaCl_2 solutions, the force is attractive at the mica-electrolyte interface below 1 M. Interestingly, the force at the silica- CaCl_2 interface is significantly less attractive compared to the force at the mica- CaCl_2 interface (Figure 4.8B).

Figure 4.8. Force gradient (N/m) versus separation (nm) measured at a mica (-) and silica (--) substrate in pure water and in 50 mM CaCl_2 solutions using the same AFM tip. B. Numerical integration of the force gradient led to the force (nN) versus separation (nm). C. Forces (nN) versus separation (nm) minus the calculated van der Waals interaction.

The force shown in Figure 4.8C is the result of subtracting the van der Waals contribution. The resulting force is attractive at the mica- CaCl_2 interface, while the force is repulsive at the silica- CaCl_2 . This result shows that the sign and magnitude of the monotonic contribution to the short-range force is influenced by the substrate in the presence of CaCl_2 salt. Supplementary Figures 4.2 + 4.3 show hydration forces measured in 1, 10, 100, 1000 mM of CaCl_2 solutions at a silica substrate. The force does not show significant deviations as a function of concentration: the force is repulsive in all concentrations studied and the oscillatory part of the force remains stable and thereby does not show large variations in amplitude or periodicity. Thus, the hydration force at silica surfaces is not significantly affected by the presence of Ca^{2+} . We have studied the hydration force at silica surfaces in more detail, the result and the discussion on this topic is presented in Chapter 5.

One can think of several explanations for the attractive short-range force, such as depletion interactions or ion-correlations.³⁸ However, the forces measured here were acquired using sharp probes (1.25 nm radius), therefore it is very unlikely that depletion interactions are at play. In addition, both depletion attraction and attraction due to ion-correlations increases with salt concentration^{38, 41}, while the forces presented here are attractive at lower concentrations and repulsive at 1 M. As pointed out in the discussion above, we try to explain the observed attractive force based on the model by Marcelia and Radic¹¹. They propose that the short-range force can be described by the modification of water near surfaces by introducing an order parameter that describes the local structure of the liquid,¹¹ that has opposite values at two identical surfaces, resulting in antisymmetric profiles. The forces associated with antisymmetric ordering are repulsive and decays exponentially. Therefore, the force can be attractive in case of symmetric ordering, as found between non-identical surfaces. Following this reasoning: the orientation of water molecules can be opposite on the silica tip and the mica surface, with respect to the surface, resulting in an energetically more favorable interaction upon approaching surfaces, since the water molecules do not have to re-orientate upon overlap. While, the orientation of water molecules at silica

surfaces (substrate and tip) are the same, upon overlap, the water molecules need to re-orientate which is energetically less favorable resulting in a repulsive force. The used silica AFM probes here and the silica surface are not truly symmetric when one considers the geometry of the system. The probe is hyperbolic and the surface is a plate. In addition, we measure an attractive short-range force in the presence of certain divalent ions, at certain concentrations. Clearly, the molecular picture of the short-range hydration force as measured here is far more complicated than the forces from a mean-field model where the interacting force is described by an order parameter. The specific cation, the valence, the salt concentration and the substrate all influence the sign and magnitude of the monotonic contribution to the hydration force.

The fact that the short-ranges forces can be attractive will be important for the interpretation of results in many systems. Firstly, one could think of the implications for colloidal instability that cannot be explained by van der Waals interactions, or the enhancement of absorption of molecules at surfaces in the presence of divalent ions, which cannot be explained by the idea of bridging due to double charges.³⁰ Furthermore, both our present and our previous work show that the layering of water molecules at the mica surface is quite robust. In a range of a few mM to a few M of salt, the oscillatory hydration force is stable where only small variations are observed. Even at silica substrates we have measured oscillatory hydration forces in the presence of different concentrations of divalent containing salt solutions and in purified water. Unlike the oscillatory contribution to the hydration force, the monotonic contribution is significantly affected by the valence of the ion, the concentration or the size of the ion. These findings indicate that there is a difference in origin of the two contributions to the hydration force.

4.4 Conclusion

We have studied hydration forces at mica and silica substrates in the presence of several divalent-chloride salt solutions over a large range of concentrations. Hereby we focused on the effect of divalent ions of different hydration energies, where we looked into the oscillatory and the monotonic contribution to the hydration force. We demonstrate that the intrinsic oscillatory hydration force at the mica-water interface is not

suppressed when divalent ions are present and show that the oscillatory hydration force is present as well on silica surfaces. Specific details of the oscillatory part of the force are affected by ion adsorption, but it remains stable over a wide range of concentrations and in the presence of different types of divalent ions, in contrast to what was found for different types of monovalent ions. Interestingly, we find that the oscillatory-suppressing effect of Cs^+ is not found if there are also Ba^{2+} ions present in solution, up to the point where there are significantly more Cs^+ in solution compared to Ba^{2+} .

While the oscillatory force is largely unaffected (except for the effect of Cs^+ ion), the hydration repulsion found at mica-water interfaces becomes attractive in the presence of divalent cations. While attractive up to around 100 mM of salt, the monotonic hydration force becomes slightly repulsive at high salt concentrations (1 M). Furthermore, we show that the magnitude and sign of the hydration force is not only affected by the type of ion present, but also by the substrate.

4.5 Supplementary information

4.5.1 Calculation Work

To interpret the force measurements, we calculate the work performed by the tip upon approaching the sample by integrating the force curves. The data presented in blue symbols in Figure 4.6 is the result of the integral of the force curves presented in Figure 4.5, from infinity (bulk) to 0.1 nm from the surface. The reason for this cut-off of 0.1 nm is clear from the Figure 4.7; very close to the surface, the interaction force is repulsive due to hard-wall contact which will result in more negative values of the total work. That part of the curve is not of physical interest; therefore, it was cut-off from the calculation. The van der Waals contribution which was subtracted from the work values (as presented in the red symbols in Figure 4.6) was also calculated till 0.1 nm from the surface.

Information on how the van der Waals force was calculated and subtracted can be found in Chapter 2.

4.5.2 Supplementary figures

Supplementary Figure 4.1. Force gradient (individual measurements in colors (>100), averaged in black) and corresponding force (red, dotted line) versus separation (nm) measured at the mica-water interface.

Supplementary Figure 4.2. Force gradient (individual measurements in colors (>100), averaged in black) and corresponding force (red, dotted) versus separation (nm) measured at the silica-electrolyte interface in several concentration of CaCl_2 .

Supplementary Figure 4.3. Force gradient a and corresponding force b versus separation (nm) measured at the silica-electrolyte interface in several concentration of CaCl₂.

Supplementary Figure 4.4. Force gradient (individual measurements in gray (>100), averaged in black) and corresponding force (red, dotted) versus separation (nm) measured at the mica-electrolyte interface in several concentration of MgCl_2 , CaCl_2 and BaCl_2 .

Supplementary Figure 4.5. Force gradient ($-dF/dz$ (N/m)) and force (nN) versus apparent separation (nm) measured in 1, 10, 100 and 1000 mM of MgCl₂ at a mica substrate.

Supplementary Figure 4.6. Force gradient ($-dF/dz$ (N/m)) and force (nN) versus apparent separation (nm) measured in 1, 10, 100 and 1000 mM of CaCl_2 at a mica substrate.

Supplementary Figure 4.7. Force gradient ($-dF/dz$ (N/m)) and force (nN) versus apparent separation (nm) measured in 1, 10, 100 and 1000 mM of BaCl₂ at a mica substrate.

Supplementary Figure 4.8: Calculated interaction force decomposed of an electric double layer, van der Waals and monotonic hydration interaction between mica and a 5 (a) and 1 (b) nm radius silica AFM tip.

4.6 References

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THE EFFECT OF THE SUBSTRATE

In this chapter we present the study on hydration forces at two different substrates: mica and silica differ in chemistry but also in roughness. Mica is atomically smooth after cleavage, while the used thermally grown silica surfaces are not crystalline in nature. We have studied the hydration force on mica and silica in a variety of aqueous solutions of mono- and divalent cations at variable pH. For both substrates, force curves were measured that were described by a monotonically decaying as well as an oscillatory contribution. The oscillatory force is the result of the modulation of the density of water molecules beneath the AFM tip due to interface-induced ordering, and here we show that the oscillatory force is present at both mica and silica, and that this contribution to the force is rather robust. As reported previously in the case of mica, Cs^+ ions behave differently from other cations: they fully suppress the force oscillations and induce an overall attractive force. The monotonic contribution to the force does show variations between the two surfaces but generally, the hydration forces at mica and silica surface show to be remarkably similar, which points to fundamentally similar hydration interactions at both surfaces.

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5.1 Introduction

Hydration forces are ubiquitous in biology and chemistry, and remain a central issue in many fields concerned with forces between surfaces, such as protein stability,^{1,2} catalysis,^{3,4} colloidal interactions in paint industry,⁵ wetting transitions relevant in oil recovery,^{6,7} and in membrane science for filtration technologies⁸. Experimentally, the hydration force was first measured between phospholipid multi-bilayers in terms of pressure-distance curves⁹, and later for individual bilayers by the use of the surface force apparatus (SFA).¹⁰ Since the pioneering works from Pashley and Israelachvili, the hydration force between mica surfaces has been studied intensively.¹¹⁻¹³ Repulsive hydration forces were measured that were attributed to the dehydration of adsorbed ions as they were removed from the surfaces at small separations.¹¹ Dehydration is enthalpically unfavorable, and thus results in a short-range repulsive force. This idea was supported by the observation that the largest magnitude of the force was measured in the presence of the smallest, most hydrated cation.¹¹ Interestingly, a reversed trend was found in studies between silica surfaces where the largest magnitude of the hydration force was measured in the presence of the largest, less hydrated cations (pH 6).¹⁴ Contrary to the hydration force measurements between mica surfaces,¹³ no oscillatory hydration force was measured between silica surfaces, only a monotonically decaying short-range force is reported. It was proposed that the layers of water molecules that result in the oscillatory contribution to the hydration force, are smeared-out at silica surfaces due to their rough nature. Consequently, it was suggested that the origin of the hydration forces is not unique, but surface specific.¹⁵

Marčelja and Radic proposed a mean-field theory to describe the monotonic hydration force.¹⁶ According to this model, interfaces interact via the order that they induce on the water film near surfaces. This order, as a result of local surface fields that orient the water molecules, is described by an order parameter that vanished in the bulk. The order parameter has opposite values at two identical surfaces, resulting in antisymmetric profiles. The forces associated with antisymmetric ordering is repulsive and decays exponentially. Such a mean-field model elucidates some aspects of measured force curves, but it does not capture the full

complexity of the hydration forces such as ion specific effects,¹⁷ the influence of the surface chemistry¹⁸, roughness¹⁹, or the influence of pH.²⁰ As shown by *e.g.* MD simulation, the hydration force is not caused by water orientation effects alone, but by the direct surface interaction and the water-mediated interaction.²¹

More recent experimental studies that focus on hydration forces make use of very sharp tips available for Atomic Force Microscopy (AFM). Using sharp probes allows to map the hydration structure in 3D^{22, 23}, or to study the evolutions of atomic-scale steps²⁴ or track individual ions at interfaces.²⁵ The oscillatory contribution to the hydration force is reported in these studies, where 3D maps show the layered interfacial structure at calcite^{24, 26} and mica surfaces²⁷. However, the monotonic contribution to the hydration force is largely ignored, but it has been measured between sharp AFM tips and mica surfaces in other experiments.^{17, 28} The monotonic contribution typically decays over 2 nm from the surface, which is longer than then decay of the modulation of the density of the water molecules.²⁹ It is challenging to disentangle the DLVO interactions from the hydration force, therefore it is more common to describe the hydration force based on its monotonic and oscillatory contribution without trying to identify the origin of the monotonic contribution to the force.²⁸ As a result, the origin of the hydration force, and the influence of the surface, remain unclear. Specifically, how does a difference in surface chemistry, atomic structure, roughness and a different pH dependence, affect the hydration force? Silica's surface charge is pH dependent due to the silanol (Si-OH) surface chemical groups.¹⁹ Mica on the other hand is a type of phyllosilicate, exhibiting a two-dimensional sheet structure. Isomorphous substitution of Al³⁺ for Si⁴⁺ results in a permanent negative surface charge, independent of pH.³⁰ Moreover, mica is atomically smooth upon cleavage, while the thermally grown silica surface (as used in this study) is amorphous and exhibits roughness on the nm length scale. Due to all these differences, it is interesting to compare hydration forces measured at these two surfaces.

In our previous work on mica (described in Chapter 3 and 4) we have studied the hydration force where we describe the force by its monotonic and oscillatory contribution. We have shown that the oscillatory

contribution is rather robust. The monotonic contribution to the force is influenced by the specific ions and its magnitude is concentration dependent in the presence of divalent cations. From this work, we have learned that the oscillatory hydration force is present at mica surfaces in the absence of salts, and that it is only suppressed in the presence of bulky ions such as Rb^+ and Cs^+ . In addition, we have shown that the monotonically decaying short-range force can be attractive in certain conditions. By measuring these forces using sharp AFM tips, we provide new insights on the influence of ions on both contributions to the hydration force. Here we follow up on that work and address the question of the influence of the substrate on the hydration force, and thereby to what extent the hydration force is surface specific. As in Chapter 3 and 4, we address these questions by discussing the oscillatory and the monotonic contribution to the hydration force. We demonstrate that the oscillatory contribution to the hydration force is present at mica and silica surfaces, and show a very similar response on the presence of ions. Generally, the hydration forces seem strongly affected by the type of ions present, and only weakly dependent on the surface.

5.2 Methods

5.2.1 Experimental preparation

Mica and silica substrates were glued using epoxy to a puck which is magnetically clamped to the piezo stage of the AFM (Asylum Research Cypher). The mica was cleaved with adhesive tape before each experiment. The silica substrates were cleaned with ethanol and isopropanol, cleaned twice using an ultra-sonication bath for 20 minutes, after which the substrate was rinsed again with ethanol and isopropanol and lastly, placed in a plasma cleaner (PDC-32G-2, Harrick Plasma) for 20 minutes. The silica substrate was glued to the magnetic puck after the cleaning procedure, while the mica was cleaved after being glued to the puck. Each AFM experiment started by flushing the system with purified water (Millipore, resistivity $18.2 \text{ M}\Omega\text{cm}$). The electrolyte solutions were prepared by dissolving the salts (LiCl , KCl , CsCl , CaCl_2 , BaCl_2 98% purity) in purified water. The pH is controlled and set to 3, 6 or 9 by either

adding NaOH or HCl to the solution. All chemicals used were purchased from Sigma Aldrich and were used without further purification.

5.2.2 AFM force spectroscopy

A schematic representation of the fluid cell is presented in Figure 5.1 that shows that the cell is not fully emerged in fluid. AFM images of a mica and a silica substrate are given, both were obtained while imaging in purified water. While imaging the atomically smooth mica surface, we can find the atomic lattice of the material: the characteristic hexagonal appearances that arises from the quasi-hexagonal arrangement of tetrahedral silica layer and the octahedral aluminum layer. The silica surface is not atomically smooth and hence we cannot resolve a lattice structure. The roughness of the used silica surfaces was found to be ~ 0.5 nm.

Figure 5.1. Schematic representation of the side view of the liquid cell. The substrate (mica or silica) is glued to a magnetic puck which is magnetically clamped to the piezo stage. The liquid cell is not fully filled with fluid. The AFM probe is fully emerged in the droplet. AFM images of the mica and silica surface in water are given. A Fourier filtered image of the mica lattice is shown in the inset which shows the characteristic hexagonal lattice. The silica surface is not of crystalline nature. The average roughness of the silica surface in this image is 0.5 nm.

The experimental force curves were fitted to the following equation:

$$\frac{dF}{dz} = \sqrt{(2\pi\sigma)^2 + \frac{1}{\lambda_{osc}^2}} A_{osc} \cos(2\pi\sigma z - \varphi - \text{atan}(2\pi\sigma\lambda_{osc})) e^{\frac{-z}{\lambda_{osc}}} + \frac{A_m}{\lambda_m} e^{\frac{-z}{\lambda_m}} \quad (5.1)$$

where A_{osc} and A_m are the magnitude of the structural and the monotonic forces, φ is the phase shift, σ is the structural hydration frequency, and λ_{osc} and λ_m are the decay lengths of the structural and monotonic force. $\frac{1}{\sigma}$ corresponds to the size of the molecule that is packed near the substrate. More information on the fitting procedure, AFM experiments, data analysis and the van der Waals calculations can be found in Chapter 2.

5.3 Results

5.3.1 Salt concentration dependence

Hydration forces were measured at the mica- and silica-electrolyte interface using sharp, silica AFM probes. Figures 5.2 shows the force gradient ($-dF/dz$ (N/m)) versus apparent separation (nm) at a silica and mica substrate in purify water and in 1, 10, 100 and 1000 mM of CaCl_2 solutions. The data acquired at the mica substrate is presented in Chapter 4 as well. Here, we show the data again for comparison with the data acquired at a silica surface. The gray, thin lines show individual measurements, the thick black line is the averaged curve and the dotted red line is the fit to this line using equation 5.1. By fitting the data, we can characterize the parameters of both the oscillatory and the monotonic contribution to the force. The force gradient measured at the mica and silica substrate displays an oscillatory character with a periodicity of ~ 0.25 nm, which is comparable with the size of a single water molecule and thus points to a layered arrangement of water molecules. The oscillatory hydration force is measured at the silica- and mica-water interface, where no ions are present. Previous studies have demonstrated that ion concentration plays an important role in the presence and magnitude of the hydration force at silica and mica surfaces.^{11, 31} Figure 5.2 shows that

the oscillatory hydration force is not significantly impacted by the presence of CaCl_2 , up to 1 M of salt. The periodicity of the structural force remains to be ~ 0.25 nm, even in salt solutions of 1 M. This is found for the structural hydration force at both surfaces. Thereby, the oscillatory hydration forces at the mica and silica substrate are very robust: the presence of Ca^{2+} ions do not impact the oscillatory hydration force significantly since the force remains very similar to the force measured in purified water.

Figure 5.2. Force gradient (N/m) versus apparent separation (nm) measured at the silica-water and electrolyte interface in CaCl_2 solutions of 1, 10, 100 and 1000 mM. Gray, thin lines are individual measurements, the thick, black line is the averaged curve and the red, dotted line is the fit (equation (5.1)). The pH of all solutions was set at 6.

The similarities points to a similar origin of the oscillatory force. The monotonic contribution to the force gradient measured at the silica surface is very weak: we do not observe large variations in the magnitude of the force gradient in the several salt concentrations studied here. The total force, the numerical integral of the force gradient (Supplementary Figure 5.1) is repulsive in all concentrations at the silica surface and does not show significant variations in magnitude. The force gradients measured at the mica substrate does show a variation in sign and magnitude. From the force gradient presented in Figure 5.2, it is clear that the force becomes more attractive upon increasing the concentration of CaCl_2 up to 100 mM. In 1 M of salt, we measure a slightly repulsive force. The effect of divalent ions on the force gradient measured at the mica substrate has been discussed in detail in Chapter 4. Here we show that the oscillatory contribution to the force gradient seems similar at the mica and silica substrate in several salt concentrations, while the monotonic contribution to the force gradient does show a different behavior on both surfaces.

5.3.2 Specific ion effects

In chapter 3 and 4 we have shown that the type of ion influences the hydration forces at mica substrates. To examine ion specific effects at silica, forces were measured in LiCl , KCl , CsCl , CaCl_2 and BaCl_2 in solutions of 50 mM at silica surfaces. The data is presented in the left column of Figure 5.3 and 5.4, where Figure 5.3 shows the effect of monovalent ions (LiCl , KCl , CsCl) on the hydration forces at mica and silica while Figure 5.4 shows the effect of divalent ions (CaCl_2 and BaCl_2). The pH of all solutions was set at 6. We choose to work in 50 mM salt solutions since force spectroscopy measurements show that the surface charge of silica is lowered by 0.1 e/nm^2 in the presence of 50 mM of monovalent salts due to ion adsorption^{6, 32, 33}, hence we know that ions are present at the silica surface at this salt concentration. In addition, we have calculated the ion coverage using the mass action model.¹¹ The result for the different alkali ions is given in Supplementary Table 5.1. The data show that the adsorption sides of both mica and silica are largely covered by ions in solutions of 50 mM. To be able to study the differences and similarities of the hydration forces of mica and silica surfaces, we have

performed the same measurements on a mica substrate, while using the same salt solutions and the same AFM tip.

Figure 5.3. Force gradient ($-dF/dz$ (N/m)) versus apparent separation (nm) measured in purified water, 50 mM of LiCl, 50 mM KCl, 50 mM CsCl at a silica (left column) and mica substrate (right column). The pH of all solutions was set at 6. Gray, thin lines are individual measurements, the thick, black line is the averaged curve and the red, dotted line is the fit (equation (5.1)).

Figure 5.4. Force gradient ($-dF/dz$ (N/m)) versus apparent separation (nm) measured in 50 mM of CaCl_2 and 50 mM BaCl_2 at a silica (left column) and mica substrate (right column). The pH of all solutions was set at 6. Gray, thin lines are individual measurements, the thick, black line is the averaged curve and the red, dotted line is the fit (equation (5.1)). This data is collected with the same AFM probe and substrates as the data presented in Figure 5.3.

As was found on mica surfaces (discussed in Chapter 3 and reproduced here), the presence of Cs^+ ions suppress the structural hydration forces at silica surfaces, while it remains stable in the presence of smaller alkali ions and divalent ions. In the presence of Li^+ , K^+ , Ca^{2+} and Ba^{2+} , the force gradient at silica surfaces show pronounced oscillatory behavior. As already observed the studies presented in Chapter 3 and 4, the force gradient measured at the mica-water interface displays pronounced oscillatory behavior. Here, we reproduce the finding that the Cs^+ suppresses the oscillatory hydration force, while it remains stable in the presence of Li^+ , K^+ , Ca^{2+} and Ba^{2+} .

In this chapter we do not focus on discussing the details of the effects of the ions on the mica substrate, but use mica as a reference for the study of the hydration force at silica surfaces. When comparing the force

gradients measured at the silica and mica substrate, we find that, generally, the short-range forces measured in pH 6 are strongly affected on the ion type, and only weakly dependent on the substrate, with a few exceptions. Both at mica and silica surfaces, the oscillatory hydration force is measured in purified water. The oscillatory hydration force is very similar on both surfaces, and also respond in a similar manner on the presence of specific ions.

The oscillatory hydration force was quantitatively described by the amplitude of the first oscillation, which is a measure of the stability of the hydration layer. The amplitude of the first oscillation of the structural contribution to the force was calculated from the fit parameters, obtained by fitting the data to equation (5.1). Supplementary Figure 5.5 shows the amplitudes of the first oscillation of the structural contribution to the hydration force extracted from the data presented in Figure 5.3 and 5.4 in open symbols. The experiment data was reproduced while using a different tip (force gradients are presented in Supplementary Figure 5.2 and 5.3), from which the amplitudes were extracted as well. The amplitudes found in the second experiment are shown in Supplementary Figure 5.5 as closed symbols. The data shows that the amplitude of the first oscillation found in purified water is very similar at the mica and silica substrate, but shows a different dependence on the type of ion present in solution. These differences are not directly clear from the total force gradient due to the monotonic contribution to the force. Supplementary Figure 5.6 + 5.7 show the total fit and the individual contributions (monotonic and oscillatory) of two curves, from which the differences in amplitude of the oscillatory contribution is more clear. The absolute values of the amplitudes are not the same in most conditions in the two experiments (Supplementary Figure 5.5). However, the trends in amplitudes as a function of ion type were reproduced in the two experiments, and the standard errors are significantly lower compared to the variations in amplitudes.

The data presented in the previous figures was acquired in solutions of pH 6. The surface chemistry of silica is pH dependent, where the isoelectric point in water is between pH 2 and 4.¹⁹ Several studies report specific ion effects that reverse upon switching the bulk pH of the

solvent.³⁴⁻³⁸ To extend our study on the effect of specific ion effects on hydration forces at silica and mica surfaces, we have measured the hydration forces in LiCl, CsCl and BaCl₂ solutions (50 mM) of pH 3 and 9.

Figure 5.5. Force gradient ($-dF/dz$ (N/m) versus apparent separation (nm) measured in 50 mM LiCl, 50 mM CsCl and 50 mM BaCl₂ (pH 3) at a silica (left column) and mica substrate (right column). This data shown here is collected using the same AFM probe as the data presented in Figure 5.6. The gray, thin lines are individual measurements, the thick, black line is the averaged curve and the red, dotted line is the fit (equation (5.1)).

Figure 5.5 and 5.6 show the data acquired at the silica- and mica-electrolyte interface in solutions of pH 3 and 9, respectively. The data presented in these figures was measured with the same AFM tip and substrates. Individual measurements are given in thin, gray lines, the thick, black line is the averaged curve and the red, dotted line is the fit (equation (5.1)). The data measured in solutions of pH 3 (Figure 5.5) shows that the structural hydration force remains stable in BaCl_2 and LiCl solutions, both at mica and silica surfaces. As was found in solutions of pH 6, Cs^+ ions suppress the structural hydration force at mica and silica surfaces. The oscillatory hydration forces at mica and silica are very similar and respond in a similar manner on the specific ions present. Also, in solutions of pH 3, the force is overall attractive in CsCl solutions, both at the mica and silica surface. The periodicity of the oscillatory force remains to be ~ 0.25 nm in solutions of pH 3, for all salts studied here.

Figure 5.6 shows the force gradients measured at the silica- and mica substrate in solutions of pH 9. The diffuse layer charge of silica surfaces is 0.06 e/nm^2 more negative in pH 9 compared to pH 3 (in 10 mM of salt solution, where is diffuse layer charge is -0.12 e/nm^2 at pH 9).³⁹ Our data shows that a change in bulk pH from 3 to 9 does not impact the structural hydration force significantly at silica or mica substrates. The magnitude of the force gradients is not significantly different from the data measured in solutions of pH 3 or 6. We find that the structural hydration force at the mica surface is stable in LiCl and BaCl_2 solutions of pH 3. The amplitude of the first oscillation at the mica- Ba^{2+} interface is found to be higher in a solution of pH 3, compared to pH 9, which is found as well at the silica surface (Supplementary Figure 5.8). In LiCl solutions, the amplitude of the first oscillation at both surfaces are higher in pH 9 compared to the amplitude found in solutions of pH 3. As was found in solutions of pH 3 and 6, the oscillatory hydration force is suppressed in the presence of CsCl solutions of pH 9. Interestingly, the overall force is repulsive at the silica surface in CsCl solutions of pH 9, while the force is attractive at mica substrates in CsCl solutions, independent of pH.

Figure 5.6. Force gradient ($-dF/dz$ (N/m)) versus apparent separation (nm) measured in 50 mM LiCl, 50 mM CsCl and 50 mM BaCl₂, (pH 9) at a silica (left column) and mica substrate (right column). This data is collected using the same AFM probe as the data presented in Figure 5.5. The gray, thin lines are individual measurements, the thick, black line is the averaged curve and the red, dotted line is the fit (equation (5.1)).

In order to study the influence of the substrate on the interacting force, the force gradient as presented in Figure 5.3 and 5.4 was numerically integrated to obtain the force (nN). The result is presented in Figure 5.7, displaying the force measured at the mica- and silica-electrolyte interface measured in pH 6. The force at mica and silica substrates in the same salt solution show to be very similar, with a few exceptions.

Figure 5.7. Force (nN) versus apparent separation (nm) after subtraction of the calculated van der Waals interaction force, at mica and silica substrates measured in purified water, LiCl, KCl, CsCl, CaCl₂ and BaCl₂ (50 mM, pH 6). The van der Waals force between the tip ($R=1.25$ nm) and mica/silica substrate is presented in the CsCl sub-figure. A Hamaker constant of $3.7e-21$ J (mica-silica) and $2.97e-21$ J (silica-silica) were used.

In the presence of Cs⁺ and Ca²⁺ ions, the force in solutions of pH 6 is repulsive at the silica substrate and attractive at the mica substrate. In the presence Li⁺, K⁺ and Ba²⁺, only small differences between the two substrates are found. In all salt solutions (of pH 6), the force is slightly

more repulsive at the silica substrate compared to the force measured at the mica substrate. The largest magnitude of the repulsive force is found in LiCl solutions, at both surfaces. At both mica and silica, the magnitude of the force decreases and ultimately becomes overall attractive as follows: $\text{Li}^+ > \text{K}^+ > \text{Cs}^+ > \text{Ca}^{2+} > \text{Ba}^{2+}$. The force is overall attractive at the mica-electrolyte interface in CsCl, CaCl_2 and BaCl_2 solutions, while the overall force at the silica surface is only attractive in BaCl_2 solutions.

5.4 Discussion

One of the first striking observations presented in this work, is the pronounced oscillatory character of the force gradient measured at the silica substrate, that is found without the addition of salts and does not show significant variations when adding salt (up to 1 M, excluding CsCl). Both at mica and silica surfaces, the oscillatory hydration force is measured in purified water and the periodicity is ~ 0.25 nm. Oscillatory hydration forces were also measured on mica surfaces in several other studies.^{13, 27, 28, 40} As discussed in section 5.1, it was proposed that the repulsive hydration forces at mica surfaces arises due to the dehydration of hydrated cations, that are prevented from desorbing.^{11, 41} This was proposed based on the absence of repulsive hydration forces between mica surfaces in the absence of salts. The origin of the hydration force at silica surfaces remains a highly debated topic in literature as well. Conventionally, independent of the specific substrate, the short-range repulsive forces has been associated with the presence of a structural layer of water molecule.^{13, 19} The overlap of these hydrated layers of two surfaces give rise to the repulsion observed in many systems.^{1, 2, 42, 43} However, until now, there has been no experimental evidence of oscillatory hydration layers at silica surfaces, and as mentioned above, hydration forces between mica surfaces were only measured in salt solutions.^{19, 44, 45} The latter issue has been discussed in Chapter 3 and 4, where we show that the oscillatory hydration force is present in the absence of added salt at the mica-water interface. It was proposed that the roughness of silica surfaces ‘smears out’ the arrangement of water molecules.¹⁵ Here, we have demonstrated that the short-range forces at the silica-water interface do show pronounced oscillatory behavior. Moreover, unlike what has been reported using colloidal force

spectroscopy, the periodicity of the oscillatory hydration force does not indicate to ion pairing ($0.6 - 0.9$ nm)³¹, but rather points to water layering (~ 0.25 nm). What is different in the current experiments? Firstly, we probe the substrate using very sharp tips. Simulations of the hydration structure (in the absence of a tip) were in striking agreement with experimental AFM data acquired using very sharp tips, which points to the strong correlation between force profiles and the intrinsic hydration layers structure in the absence of a tip.⁴⁶ This agreement between simulation (without including a tip) and experimental data can only be acquired when measuring the forces using sharp probes. Figure 5.1 shows that the silica surfaces used in this study are rough (not atomically smooth), unlike the mica surface from which we can resolve the atomic lattice. Since we do measure oscillatory hydration forces, even though the silica surface is rough, we propose that the roughness of the larger colloidal probes used in older AFM studies smear out the oscillatory structure, not the surface itself.^{47, 48} Secondly, the geometry of our experimental system is different from the SFA and colloidal force spectroscopy. The sharp tip does not induce lateral confinement, unlike colloidal probes and SFA. The direct comparison of SFA, or colloidal force spectroscopy with AFM (where sharp tips are used) is therefore unsuitable, since the perturbation of the system will determine the outcome.

As was found on mica surfaces presented in Chapter 3, the presence of Cs^+ ions suppress the structural hydration forces at silica surfaces, while it remains stable in the presence of Li^+ , K^+ , Ca^{2+} and Ba^{2+} . Complementary MD simulations of the mica-electrolyte interface show that the density of water molecules is lower in the presence of Cs^+ ions at the surface, which leads to the absence of an oscillatory force profile.¹⁷ Within the experimental conditions that we have studied, only the presence of Cs^+ and Rb^+ , which are known to have a lower hydration energy compared to the other alkali and divalent cations⁴⁹, suppresses the structural hydration force at silica and mica substrates. Therefore, we can conclude that the oscillatory hydration force at these surfaces is very robust and that its origin is the same for both surfaces: the modulation of the density of water molecules beneath the tip due to interface-induced ordering. This is

schematically represented in Figure 5.8C, where we show the TEM image of the used AFM tip and a drawing of the solid-electrolyte interface. The hydrated AFM tip approaches the solid-liquid interface where the surface induces a layered arrangements of water molecules.

Figure 5.8A. High resolution TEM image of a used AFM probe. The semi-major axis is indicated by the thick white line between the end of the tip and the crossing of the dotted lines that follow the hyperbolic shape of the tip. The gray area around the tip is manually edited, the reason for this is clear from figure 5.8B: Zoomed-out TEM image of the same probe, that shows a layer of glue on one side of the probe which is attached in the process of preparing the TEM sample. C: Schematic presentation of the force spectroscopy measurement at the solid-electrolyte interface.

Another striking observation is the similarity of the structural hydration force measured at the mica and silica substrate. When comparing the force gradient measured at these substrates in pH 6 (Figure 5.3 and 5.4), we find that, generally, the short-range forces strongly depend on the ion type, and

only weakly depend on the substrate, with a few exceptions. Only in the presence of CsCl and CaCl₂ we find significant different forces at the mica and silica surface, where the total force is repulsive at the silica surface, while attractive at mica. When comparing the AFM images given in Figure 5.1, it is quite remarkable that the hydration forces are so similar since the surfaces are very different. To understand this, we looked into the coverage of adsorbed ions on mica and silica surfaces in the salt concentration used in this study (50 mM). We have calculated the ion coverage using the mass action model¹¹, which takes into account the finite sizes of the adsorbed hydrated ions. Cation adsorption pK values on mica were obtained from Pashley's experimental data, and on silica from Chapel's experiments.¹⁴ The presented coverage is the percentage of charged sites that is occupied by an ion. The result is given in Supplementary Table 5.1. The calculated coverages (%) show that both mica and silica are largely covered by cations in 50 mM of salt solutions. Based on these rough calculations, the total ion coverage on mica and silica is very similar. Note that these values merely offer a good relative estimation, but cannot be interpreted as accurate absolute values, since SXRD measurements have shown that Cs⁺ occupancy is ~ 45 % on mica surfaces in 50 mM of salt solution,⁵⁰ while the calculation given here result in occupancies of around 90%.

The pH of the solvent influences the protonation state of silica surfaces, where the isoelectric point in water is between pH 2 and 4.¹⁹ Interestingly, our data shows that the structural hydration force at the silica substrate is not largely impacted by the bulk pH between pH 3 and 9. Cunlu et al. analyzed experimental AFM data and quantified equilibrium constants for the deprotonation of silanol groups and for the adsorption of Na⁺ and K⁺ cations through surface complexation modelling.⁵¹ The authors suggest that the deprotonation of silanol groups increases towards pH 9, but that the total surface charge remains moderate due to cation adsorption.⁵¹ Assuming that we measure through the Stern layer, we find that the interaction force at the silica surface is not significantly altered by pH up to 9. This is in line with a recent study where it is shown, by MD simulations, that the density of water near a silica surface is nearly independent of surface charge (and salt concentration).²⁹ In addition, the

authors inferred the surface potential by measuring second harmonic scattering and show that it varies little as a function of pH (between 5.5 and 10). Only at pH 11, the surface potential of silica shows a significant drop due to the deprotonation of silanol groups.²⁹ Thus indeed, in solutions of pH 9, as used in our measurements, the surface potential is not significantly different from the surface potential found in pH 6.

The monotonic contribution is found to be different at mica and silica surfaces in certain conditions, but generally shows to be remarkably similar. The sharp AFM tips we use are not sensitive to the electrostatic contribution of the DLVO force. As discussed in Chapter 3 and 4: if the force was dominated by continuum electrostatics, its range would be determined by the Debye screening length and thus vary with salt concentration. The forces show no variation in decay length as a function of salt concentration (Supplementary Figure 5.1). The van der Waals contribution was calculated and subtracted from the total force such that we can compare the resulting forces to the forces presented in the previously discussed papers^{11, 12, 14} (that also present the hydration force, which was calculated by subtracting the DLVO forces from the total force that was measured). The result is presented in Supplementary Figure 5.9 and the details of the subtraction of the van der Waals calculation are described in Chapter 2. The van der Waals contribution to the force is very similar at the mica and silica surface (as shown in the CsCl sub-figure in Figure 5.7). Therefore, subtracting the van der Waals does not significantly impact our observations based on the total force.

How do the hydration forces measured in this work fit into the picture sketches based on the older SFA experiments? As discussed in section 5.1, SFA experiments have shown that the greatest magnitude of the monotonic hydration force between silica surfaces is found in pure water, and that the repulsion is reduced in the presence of salt.¹⁴ The reduction in magnitude is correlated to the size of the cation: the more hydrated the ion, the weaker the force.¹⁴ A reversed trend was found between mica sheets.¹¹ As a result of these SFA experiments it has been pointed out that the origin of the hydration force is not unique in different systems,¹⁴ since it was proposed that the hydration forces between mica surfaces is the result of

the dehydration of adsorbed ions, while the hydration forces between silica surfaces was believed to be intrinsic, due to strong hydrogen bonds between water and the hydroxyl groups.

Our experimental data does not correlate with the previously described SFA measurements, where a reversal of the ion specific effect was found in a mica-mica system¹¹ compared to a silica-silica system.¹⁴ But as discussed based on the oscillatory behavior of the force gradient, the geometries of the experimental methods are different, and as a result, it is not surprising that the results have a different outcome. The use of a sharp AFM probe allows to study interactions that a nanoscale object encounters upon approaching a substrate, and is thereby a better comparison to for example interacting (bio)molecules at a surface. Our AFM data shows that the hydration forces are, generally, very similar on mica and silica surfaces: the decay length is of the same order and the effect of specific ions is similar except for a few conditions (CsCl and CaCl₂ (Figure 5.7)). The magnitude of the force is, as a function of concentration, different at both surfaces. While the force at the silica surface varies little when changing the salt concentration, the force at the mica surfaces becomes more attractive upon increasing the salt concentration, up to 1 M where the force becomes slightly repulsive (as discussed in Chapter 4). However, this experimental data was not obtained using the same AFM probe, unlike all the other data presented in the figures in this chapter. Therefore, we might not be able to directly compare the magnitudes of the forces. The monotonic contribution to the forces that are measured in this work, where the same probe was used in the same salt solutions, show to be remarkably similar, and thereby point to a similar origin.

5.5 Conclusions

Hydration forces were measured at mica and silica substrates in a variety of aqueous solutions of mono- and divalent cations at variable pH. For both substrates, similar force curves containing a monotonically decaying as well as an oscillatory part were obtained. The oscillatory force is the result of the modulation of the density of water molecules beneath the AFM tip due to interface-induced ordering, and here we show that the oscillatory force is present at both mica and silica, and that this contribution to the force is rather robust. As reported previously in the case

of mica, Cs^+ ions behave differently from other cations: they fully suppress the force oscillations and induce an overall attractive force. The orientation of water molecules, influenced by the pH and the ions adsorbed on the surfaces, is likely to result in the monotonic contribution to the force. This contribution to the force does show variations between the two surfaces but generally, the hydration forces at mica and silica substrates show to be remarkably similar, that points to fundamentally similar hydration interactions at silica and mica surfaces.

5.6 Supplementary Information

Supplementary Table 5.1: pK values and occupancy (%) for mica and silica surfaces for 50 mM salt solutions of LiCl, NaCl, KCl and CsCl. The pK values were taken from Pashely's¹¹ and Chapel's¹⁴ work, which were obtained by fitting their experimental data. The occupancy is calculated using the mass action model.^{11, 14}

Salt (50 mM)	mica		silica	
	pK	Occupancy (%)	pK	Occupancy (%)
LiCl	3	66.7	3.46	62.2
NaCl	3.5	80.2	3.25	78.9
KCl	3.5	86.3	3.3	81.9
CsCl	3.1	88.8	2.97	75.6

Supplementary Figure 5.1. Force (nN) versus apparent separation (nm) measured at a silica substrate in purified water, and in 1, 10, 100, 1000 mM of CaCl_2 . The force presented here is the result of the numerical integral of the force gradient presented in Figure 5.2.

Supplementary Figure 5.2. Force gradient ($-dF/dz$ (N/m)) versus apparent separation (nm) measured in water, 50 mM of LiCl, 50 mM KCl, 50 mM CsCl, 50 mM CaCl_2 and 50 mM BaCl_2 at a silica substrate. The pH of all solutions were set at 6. The black line is an averaged curve of > 150 individual curves.

Supplementary Figure 5.3. Force gradient ($-dF/dz$ (N/m)) versus apparent separation (nm) measured in water, 50 mM of LiCl, 50 mM KCl, 50 mM CsCl, 50 mM CaCl_2 and 50 mM BaCl_2 at a mica substrate. The pH of all solutions were set at 6. The black line is an averaged curve of > 150 individual curves.

Supplementary Figure 5.4. Force gradient (N/m) versus apparent separation (nm) measured at the mica-water interface in 4 different experiments, where different mica sheets and different AFM tips were used.

Supplementary Figure 5.5: Amplitude (nN) of the first oscillation extracted from the fit (equation (5.1)) to the data presented in Figure 5.2 and 5.3. The error bars are the standard errors of the mean of the individual force gradients.

Supplementary Figure 5.6. Fit of data measured at the silica-BaCl₂ interface (50 mM), as presented in Figure 5.4.

Supplementary Figure 5.7. Fit of data measured at the mica-LiCl interface (50 mM), as presented in Figure 5.4.

Supplementary Figure 5.8. Amplitude (nN) of the first oscillation extracted from the fit (equation (5.1)) to the data presented in Figure 5.5 and 5.6.

Supplementary Figure 5.9. Force (nN) versus apparent separation (nm) after subtraction of the calculated van der Waals interaction force, at mica and silica substrates measured in purified water, LiCl, KCl, CsCl, CaCl₂ and BaCl₂ (50 mM, pH 6). The van der Waals force was subtracted from the data presented in Figure 5.7.

5.7 References

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THE EFFECT OF ELEVATED TEMPERATURE

The interesting properties of water can be assigned to the ability to form a strong hydrogen bonded network. This network of hydrogen bonds is affected by the environmental temperature. At the mica-water interface, water molecules are packed in layers that can be measured by the use of AFM as oscillatory hydration forces. In this chapter, we have investigated the hydration force at mica-water and mica-electrolyte interfaces at elevated temperatures. So far, we have studied the influence of cations and the substrate on the hydration forces at 25°C, where we have learned that the oscillatory contribution to the hydration force is remarkably robust in the presence of mono- (except Cs^+ and Rb^+) and divalent ions. Moreover, even at surfaces that are not atomically smooth such as silica, we have measured oscillatory hydration forces. In this chapter we show that the oscillatory force profile remains stable up to at least 65°C. We have studied hydration forces at mica substrates in purified water, KCl and CaCl_2 , and show that in these solutions the oscillatory hydration force is stable and that an attractive force develops upon increasing the temperature.

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6.1 Introduction

Interaction forces play an important role in numerous phenomena, like lubrication¹, friction² and in flow in porous media³ (as in oil reservoirs) as well as in lab-on-chip applications.⁴ On small length scales, a liquid behaves differently near an interface compared to bulk fluid. An interesting phenomenon that occurs in the first few nanometers from the solid-liquid interface is the structuring of the liquid, which gives rise to the oscillatory solvation (or hydration in aqueous solutions) force.⁵ Layering occurs for entropic reasons like in a hard-sphere liquid, but it is usually also affected by liquid-surface interactions. The layering of solvent has been studied extensively using Surface Force Apparatus (SFA)⁶⁻⁷ and Atomic Force Microscopy (AFM)⁸⁻⁹.

Octamethylcyclotetrasiloxane (OMCTS) is often used to study oscillatory solvation forces due its large molecular size. The first temperature dependent experimental study was performed using OMCTS between mica sheets using SFA.⁷ The results show that between a temperature variation of 14-29°C, the range and magnitude of the solvation force are the same above and below (in super-cooled state) the melting temperature of OMCTS. On the other hand, AFM measurements in OMCTS over a wider temperature range (20-60°C) report that the oscillatory solvation force strongly decrease upon increasing the temperature.¹⁰ The authors attribute this behavior to the temperature dependent decrease in the entropic energy-barrier that the system needs to overcome when squeezing-out the layers. While the squeeze out force varies with temperature, the discrete solvation layers can be observed at all temperatures that were studied. The effect of elevated temperatures on the oscillatory solvation forces using other liquids has been studied as well. Measurements in hexadecane and dodecanol at highly oriented pyrolytic graphite are interesting due to their interaction with the surface.¹¹ Studies have shown that the configuration of these absorbed molecules is strongly temperature dependent.¹²

The influence of elevated temperatures has been studied in many systems. For example, it has been reported that a rise in temperature increases the stability of suspensions in aqueous solutions, due to the increase in entropy, making it less likely for particles to collapse.¹³ Other

examples can be found where an elevated temperature affects the physical chemical properties of the system, such as in oil recovery¹⁴, protein folding¹⁵, catalytic activities¹⁶ etc. These are all macroscopic observations, but how are the interactions forces at the smaller length's scales affected by temperature?

The hydration force is a particularly interesting force, due to the fact that water molecules form a hydrogen bonded network, and therefore has the possibility of longer-range ordering effects than would be typical of simpler non-associating liquids. As a result, next to the expected attractive van der Waals and repulsive double layer forces between two surfaces in water, the additional oscillatory force and a monotonic repulsive or attractive force can be measured that decay exponentially.¹⁷ Temperature influences the hydrogen bonded network: at higher temperatures, it is destabilized resulting in more degrees of freedom, a lower density and above 100°C, results in vapor. But how does temperature influences water on small lengths scale at an interface? Will the oscillatory hydration forces remain stable upon increasing the ambient temperature, as was found for organic solvents? Is the origin of the oscillatory hydration force and its response on the ambient temperature the same as for organic solvents?

As mentioned above, longer-ranged affects are observed in aqueous solutions, that decay exponentially. This force is termed the (monotonic) hydration force, and is reported in many different systems ranging from colloidal science¹⁸ to proteins in biological studies.¹⁹ It is known that the monotonic hydration force is affected by the type of ion present in solution²⁰, where the magnitude of the repulsive force is larger in the presence of more hydrated cations at mica surfaces. The effect of temperature on the hydration forces has not been studied in detail yet. Other experimental techniques have looked into the effect of elevated temperatures on interfacial phenomena at mica surfaces. From x-ray diffraction measurements it is known that the adsorption of ions on mica surfaces is not significantly affected by an increase in temperature:²¹ the adsorption height and the coverage of ions remains the same (within error bars) while varying the ambient temperature from 25 to 60°C. Interestingly, the authors did observe a difference in adsorption in solutions where two types of ions are present (Cs^+ and Ca^{2+}): Cs^+ has a

higher affinity to the mica surface at a higher temperature. This was explained by the differences in hydration energies. This is one of the very few studies that has addressed the effects of high temperatures on the interfacial structure of mica-electrolyte interfaces.

In this chapter we have addressed this question by measuring forces at mica surfaces in aqueous solutions by the use of AFM. By driving the AFM tip using photo-thermal excitation, the measurements are stable and the responses of the probe can be tracked in a controlled manner, making it possible to measure at high temperatures. We addressed the question if the oscillatory hydration forces remain stable at high temperatures, as was found for oscillatory solvation forces in simpler non-associating liquids. Furthermore, we address if/how the monotonic contribution to the hydration force is affected by elevated temperatures in purified water, and in the presence of a mono- and in divalent containing electrolyte solutions.

6.2 Methods

Mica substrates were glued using epoxy to a puck which is magnetically clamped to the piezo stage of the AFM. The mica was cleaved with adhesive tape before each experiment. Each AFM experiment started by flushing the system with purified water. The electrolyte solutions were prepared by dissolving the salts (KCl and CaCl_2 (98% purity)) in purified water. The pH of 50 mM of divalent salt solutions is around 5, which was adjusted to 6 by adding NaOH. All chemicals used were purchased from Sigma Aldrich and were used without further purification. The Asylum Research Cypher ES offers an environmental control chamber, where the sample stage allows heating or cooling of samples in liquid environments. In this work, we have varied the temperature between 25-65°C. The software allows to track the temperature of the liquid cell. Before changing the temperature of the closed cell, the cantilever was moved away from the surface. After the set temperature was reached, the system was equilibrated for 5 more minutes after which the measured was started. Supplementary table 6.1 shows that the drive frequency and Q factor of the AFM probe are little affected by the variation of the ambient temperature between 25 and 65°C.

The experimental force gradient curves were fitted to the following equation:

$$\frac{dF}{dz} = \sqrt{(2\pi\sigma)^2 + \frac{1}{\lambda_{osc}^2}} A_{osc} \cos(2\pi\sigma z - \varphi - \text{atan}(2\pi\sigma\lambda_{osc})) e^{\frac{-z}{\lambda_{osc}}} + \frac{A_m}{\lambda_m} e^{\frac{-z}{\lambda_m}} \quad (6.1)$$

where A_{osc} and A_m are the magnitude of the structural and the monotonic forces, φ is the phase shift, σ is the structural hydration frequency, and λ_{osc} and λ_m are the decay lengths of the structural and monotonic force. $\frac{1}{\sigma}$ corresponds to the size of the molecule that is packed near the substrate. More information on the fitting procedure, AFM experiments, data analysis and the van der Waals calculations can be found in Chapter 2.

6.3 Results

Hydration forces were measured at the mica-water interface using amplitude modulation AFM at variable temperatures. Figure 6.1 shows the force gradient measured in purified water at a mica substrate at 25°C. The gray thin lines show >200 individual measurements, the thick black line is the averaged curve. Numerical integration led to the force which is given by the black, dotted line. The force gradient shows a pronounced oscillatory character, where the distance between adjacent maxima (or minima) is ~ 0.25 nm that points to a layered arrangement of water molecules in the first nanometers from the mica surface.²² The amplitude of the oscillations increases upon decreasing the separation between surface and AFM probe: more energy is required to push through the arranged layer of solvent that is packed at the substrate. The force (black, dotted line) is repulsive at the mica-water interface at 25°C.

Figure 6.1. Force gradient ($-dF/dz$, thick black line) and force (F/R , black, dotted line where $R = 0.15$) (N/m) versus apparent separation (nm) measured in purified water at a mica substrate. B: Topographical height image of the mica-water interface. The scale bar is 2 nm. Top insets represent zooms of atomic scale images after processing with Fourier transformation and the corresponding magnitude spectrum.

Figure 6.1B shows the topographical height profile of the mica-water interface. The characteristic hexagonal lattice of the mica surface is resolved, that arises from the quasi-hexagonal arrangement of the tetrahedral silica and the octahedral aluminum layers. The inset shows a part of the same image after filtering using 2D Fourier transformation and the corresponding magnitude spectrum that shows the hexagonal lattice structure.

The ambient temperature of the fluid cell was controlled and increased to study the impact of the ambient temperature on the hydration forces at mica surfaces. Figure 6.2 shows the force gradients measured at the mica-water interface at set temperatures: 30, 40, 50 and 60°C. The left column shows the force gradient measured at the mica-water interface (purified water), the right column shows the force gradient measured at the mica surface in the presence of 50 mM CaCl_2 . All data presented in Figure 6.2 was acquired with the same probe, at the same mica substrate.

Figure 6.2. Force gradient ($-dF/dz$ (N/m)) versus apparent separation (nm) measured at the mica-water (left) and mica- CaCl_2 (right) interface at 30, 40, 50 and 60°C.

The data presented in Figure 6.2 shows pronounced oscillatory hydration forces at the mica surface up to 60°C in purified water and in 50 mM of CaCl_2 . There is no significant variation found in the periodicity of the oscillatory component in the force gradient when changing the ambient temperature. Interestingly, the total force becomes attractive upon increasing the temperature in both water and in 50 mM of CaCl_2 . As is shown in Chapter 4, the force gradient measured at the mica- Ca^{2+} interface

is attractive (up to 1 M of salt). Here we show that the force gradient, measured in 50 mM of CaCl_2 , becomes more attractive when increasing the ambient temperature. The data described was quantified by fitting the experimental data to an empirical function consisting of a combination of a monotonically decaying exponential function and a decaying oscillatory contribution, as is described in equation (6.1). The amplitude of the oscillatory contribution to the force gradient was extracted from the fit parameters, which corresponds to the energy needed to push through the individual water layers that are induced by the surface. It is a measure of the stability of the interfacial water layers. Figure 6.3 shows the amplitude of the first oscillation of the oscillatory contribution to the force gradient, extracted from the data presented in Figure 6.2, given as a function of temperature.

Figure 6.3: Amplitude of the first oscillation (N/m) found in the force gradient, extracted from the data that is presented in Figure 2, versus temperature ($^{\circ}\text{C}$). Red dots show the amplitude found in the data measured in 50 mM of CaCl_2 , the blue squares show the amplitude found in the data measured in purified water. The error bar denotes the standard error of the mean.

The data shows that the amplitude of the first oscillation increases upon increasing the ambient temperature. The increase in amplitude of the first

oscillation is found in purified water and in the presence of 50 mM of CaCl_2 .

The force gradient, as presented in Figure 6.2, was numerically integrated to obtain the force (nN). The result is presented in Figure 6.4.

Figure 6.4. Force (nN) versus apparent separation (nm) measured at the mica-water interface (left) and mica- CaCl_2 interface (right). This force is the result of the numerical integral of the force gradient presented in Figure 6.2.

In purified water and in the presence of 50 mM of CaCl_2 , the force becomes attractive upon increasing the ambient temperature, where this

effect is more pronounced in the presence of Ca^{2+} ions. The largest magnitude of attractive force was found in the presence of 50 mM of CaCl_2 at 60°C. The dotted lines in Figure 6.4 represent the force from which the calculated van der Waals force was subtracted. The van der Waals contribution to the force is very little due to the small interaction area of the sharp AFM tip (~ 1 nm radius). In all conditions the force, after subtraction of the van der Waals force, remains attractive.

In another experiment, where a different mica substrate and AFM probe was used, a similar trend was observed, as shown in Supplementary Figure 6.1): the oscillatory hydration force remains stable in purified water upon increasing the ambient temperature up to 60°C. Without the addition of ions, the total force becomes attractive upon increasing the ambient temperature. In this experiment, we have measured the hydration forces as well in the presence of 50 mM of KCl, as presented in the right column of Supplementary Figure 6.1. As in purified water and in 50 mM of CaCl_2 , the oscillatory hydration force remains stable up to 60°C and an attractive force develops, which again is more pronounced in the presence of salt compared to the forces measured in purified water. The amplitude of the oscillatory contribution to the force was extracted, the result is given in Supplementary Figure 6.2. We find that the amplitude of the first oscillation increases upon increasing the ambient temperature, in purified water and in solutions of 50 mM of KCl, as was also found in the data presented in Figure 6.3.

To further interpret the experimental observations, we calculate the work performed by the tip upon approaching the substrate which is the integral of the force curve, taken from right to left. The result is given in Figure 6.5, where the red symbols show the work values found in 50 mM of CaCl_2 solutions, the blue symbols show the work values found in purified water. The values given in square symbols contain contribution from both the hydration force and direct tip-sample forces due to van der Waals interaction. The latter was subtracted (see Chapter 2: Methods for details), the result (ΔW_m^{hydr}) is given in the triangles, which is negative for all conditions studied here, implying attractive interaction forces. The absolute value of ΔW_m^{hydr} are only a few kT. Given the strength of a H-

bond of ≈ 3 kT (without separating the molecules),²³ we conclude that the changes in the water ‘structure’ correspond to the equivalent of breaking only a few H-bonds (right axis Figure 6.5).

Figure 6.5. Mechanical work upon approaching tip and sample in units of kT/mol (left axis) and equivalent number of H-bonds (right axis) vs. temperature ($^{\circ}\text{C}$). The squares are the total work of the force, which is the integral of the force presented in Figure 6.4. The triangles correspond to the work from which the van der Waals contribution was subtracted.

6.4 Discussion

The results presented above lead to the following questions: how do the oscillatory hydration forces remain stable up to 60°C , and what drives the development of the attractive interaction force at mica surfaces upon increasing the ambient temperature, even in the absence of added salts? Firstly, we shall address the oscillatory contribution to the measured force. To the best of our knowledge, there are no reports in literature that show the influence of elevated temperature on the oscillatory hydration force, therefore, we shall look into what is reported: the effect of temperature on

solvation forces. It is reported in an AFM study where organic solvents were used (OMCTS, *n*-hexadecane and *n*-dodecanol) that the discrete solvation layers can be observed in force measurements at elevated temperatures (25-75°C).¹⁰ However, with increasing temperature there is a significant decrease in the magnitude of the measured solvation forces and a reduction in the number of solvation oscillations. The temperature effects that are observed in the study by L.T. W Lim et al (ref. 11) were not explained based on the fundamental behavior of the solvation force but by how the layers are squeezed from the tip-sample gap, which is a process that is thermally activated. This process response to temperature changes and thereby results in the variations in the magnitude of the force oscillations with temperature. More studies show that the solvation force remains stable upon increasing the ambient temperature.^{7, 24-25} In our experiments we observe, as is seen for organic liquids, that the oscillatory contribution to the force remains stable at elevated temperatures (65°C). This is an interesting finding since it shows that the polar, hydrogen bonded and dynamic water molecules, behaves similar as the organic fluids such as OMCTS. The origin of the oscillatory force is the same, the layering of the solvent, which is remarkably stable at various temperatures.

We have extracted the amplitude of the first oscillation from the oscillatory contribution of the fit (equation 6.1) to the experimental data. From the data presented in Figure 6.3 we learn that the amplitude increases upon increasing the ambient temperature. This is different from what is found in the study discussed above, where the magnitude of the force needed to squeeze out the solvation layer decreases upon increasing the ambient temperature. A possible explanations for our finding could be related to the properties of the mica surface and the water molecules: the surface potential of mica is known to increase upon increasing the temperature.²⁶ A higher surface potential and thereby surface charge, could result in a more stable hydration structure since the polar water molecules will be more strongly aligned. However, our experiments do not provide evidence of a higher surface charge, since the used sharp probes in this study are not sensitive to the electrostatic interactions.²⁷ Moreover, for extracting the amplitude of the first oscillation, we fit the

experimental data to equation (6.1) and look only at the oscillatory contribution to the force. It is unclear how and if the oscillatory and monotonic contribution to the force are correlated, therefore, looking into one contribution to the total force remains artificial.

Unlike the forces measured in organic solvents, in water, there is an additional contribution to the oscillatory solvation (hydration) force: the force can be overall attractive or repulsive, as we describe by a monotonically decaying (hydration) force. We observed an appearance of attractive forces upon increasing the ambient temperature, in all conditions studied here (in purified water, 50 mM of KCl and 50 mM of CaCl_2). As given in Figure 6.5, the work needed to approach the tip to the mica surface decreases upon increasing the temperature: it is easier to push away the solvent in the gap between the tip and substrate. Given the enthalpy of a H-bond of $\approx 3 \text{ kT}$ (without separating the molecules),²³ we can express the work (kT/molecule) in an equivalent number of hydrogen bonds (right axis of Figure 6.5). This shows that, when changing the temperature from 25 to 60°C, the required work per molecule is lowered in the order of only a few hydrogen bond energies. This is in line with other experimental studies that show that the number of hydrogen bonds per water molecule decreases by 1 or 2 in a similar temperature range,²⁸ therefore the work required in our experiments can largely be explained by enthalpic contributions. We show that in the presence of divalent cations the required work is even lower. Following the argument described above, this suggest that less hydrogen bonds are formed per water molecule in the presence of divalent cations.

We have calculated the van der Waals force between tip and the mica surface using dielectric constants and refractive indices found at several temperatures to learn how much the van der Waals force changes with temperature. The refractive indices and dielectric constants that were used can be found in Supplementary Figure 6.1. The result of this calculation is shown in Supplementary Figure 6.3, where we see that the van der Waals force does not vary significantly in the temperature range that was studied here. Therefore, we conclude that the van der Waals force, to the

best of our estimate, is not affected by the increase in temperature in the performed experiments.

The transition from repulsive to attractive interactions upon increasing the ambient temperature has been reported as well between DNA helices.³⁰ The authors of this work suggest that the attractive hydration forces are accomplished by the release of water into the bulk, which is a balance between the entropy and enthalpy of the solvent near the surface and the values in the bulk. The entropy contribution to the total energy increases with temperature, which reduces the energy needed to press the surfaces together. This could, additionally to the reduction in enthalpy (work (kT/molecule), lead to more attractive interaction forces. The presence of cations increases the magnitude of the attractive interaction force, both for K^+ and for Ca^{2+} . As discussed in Chapter 3, the presence of K^+ ions at mica surfaces does not change the magnitude or sign of the force measured over 5 nm separation at room temperature.²⁰ The presence of Ca^{2+} (50 mM) does result in attractive short-range forces at room temperature (Chapter 4). Here, we learn that the magnitude of the attractive force is more pronounced when these cations are present and when the ambient temperature is increased. We cannot distinguish between the electrostatic attractive interaction between the ions on approaching surfaces and an attractive water-mediated interaction force, but since the attractive forces are measured as well in the absence of ions, it can be argued that the water-mediated interaction force can play a dominate role.

6.5 Conclusions

We have measured forces at mica surfaces over 5 nm separation in purified water, and in 50 mM of KCl and $CaCl_2$ solutions, and show that in these solutions the oscillatory hydration force can be detected when the temperature was varied between 25 and 65°C°. This observation is consistent with other SFA- and AFM experiments performed in organic solvents. This points to a similar origin of the oscillatory behavior of the interactions in both water and organic solvents. Furthermore, we show that the interaction force in the first 5 nanometers from the mica surface develops to become more attractive upon increasing the ambient temperature. We argue that the development of the attractive force could

be due to the decrease in enthalpy energy upon increasing the ambient temperature.

6.6 Supplementary Information

Supplementary Figure 6.1. Force gradient ($-dF/dz$ (N/m)) and force (F/R , where $R = 1$ nm (N/m)) versus apparent separation (nm) measured at the mica-water (left) and mica-KCl (right) interface at 30, 40, 50 and 60°C Celsius. The thin black line is the force.

Supplementary Figure 6.2. Amplitude of the first oscillation (N/m) found in the force gradient as presented in Supplementary Figure 6.1, versus temperature (°C). Orange dots show the amplitude found in the data measured in 50 mM of KCl, the blue squares show the amplitude found in the data measured in purified water.

Supplementary table 6.1: Drive frequency (ω) and Q factor of the AFM probe measured in water and in 50 mM of CaCl_2 at varies temperatures.

water	Drive Frequency (KHz)	Q factor
30°C	452.857	4.9
40°C	459.575	5.2
50°C	462.163	5.0
55°C	471.2	5.5
60°C	462.163	5.2
50mM CaCl_2		
30°C	462.144	4.7
40°C	460.741	4.8
50°C	462.144	5.1
55°C	462.575	5.1
60°C	462.144	5.3

Supplementary Figure 6.3. Calculated van der Waals interaction force (nN) versus apparent separation (nm) for different temperatures. The dielectric constant and refractive index changes slightly as a function of temperature. Values obtained from literature at 30, 40, 50 and 60°C were used to calculate the Hamaker constant and the van der Waals interaction force. The used dielectric constants and refractive indices are given in Supplementary table 6.2.

Supplementary table 6.2: Dielectric constants (ϵ), refractive indices (n) and the Hamaker constant (calculated based on the ϵ and n) for different temperatures.³¹⁻³²

T (°C)	ϵ	n	Hamaker
25	78,3	1,3275	$8,86^{-21}$
30	76,5	1,327	$8,89^{-21}$
40	73,22	1,3257	$8,98^{-21}$
50	69,9	1,3241	$9,09^{-21}$
60	66,8	1,3223	$9,22^{-21}$

6.7 References

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CONCLUSIONS AND OUTLOOK

7.1 Conclusions

In the introduction I established that in order to understand the oscillatory hydration force and its dependence on the environmental conditions, more force data is required that can resolve the oscillatory hydration force. The aim of this work was to obtain more experimental data and thereby gain more insight into the origin of this force by describing the force with an oscillatory and monotonic contribution and by focusing on the effects of specific ions, temperature and substrate.

In Chapter 2 I found that the oscillatory hydration force can be measured at mica surfaces even in the absence of salts and that the type of ions influences the magnitude of the total force. As long as this oscillatory behavior is present, there is also a repulsive monotonic contribution acting over similar length-scales. The oscillatory contribution to the force is suppressed in the presence of bulky, less hydrated ions (Cs^+ and Rb^+) which was corroborated by complementary MD simulations. The local reduction of the water density in the vicinity of these ions was found to be crucial for this effect. In the following chapter, I found that divalent cations of different sizes, do not suppress the oscillatory hydration force: it is found in the presence of Mg^{2+} , Ca^{2+} and Ba^{2+} up to 1 M of salt. Furthermore, I also found evidence of attractive monotonic contributions to the force at some conditions. In Chapter 4 I found that the oscillatory hydration force is even present at silica surfaces that are not atomically smooth, also in a large range of salt concentrations (including no salt) and ion types. As was found at mica surface, the presence of Cs^+ ions suppresses the oscillatory force. Generally, the hydration force is remarkably similar at mica and silica surfaces: its magnitude and sign is more strongly influenced by the type of ions present than it is by substrate. Lastly, in Chapter 5, I again found how remarkably robust the oscillatory hydration force is: even at temperatures up to 60°C it can be observed at mica surfaces. Furthermore, in the absence of added salts, the monotonic contribution to the forces become even more attractive upon increasing the ambient temperature.

All these findings indicate that the oscillatory contribution to the force that was measured, at mica and silica surfaces, is really robust. By measuring these forces using sharp AFM tips, we find that the oscillatory

contribution to the force remains stable (except for the presence of Cs^+ and Rb^+ ions) and the distance between maxima (or minima) in the force gradient is not significantly different, even in the presence of 4 M of salt. This oscillatory behavior is a result of the packing of water molecules near the surface. It arises due to entropic effects, as it would in any system of hard-spheres near a wall. However, in aqueous solutions, the strong hydrogen bonded network between the water molecules, between the surfaces and solvent, and between the water molecules and the ions, result in an additional contribution.

The monotonic contribution to the force is more complex, and unfortunately no conclusive theory of why and how it arises yet exists. I found that it is affected by the type of ions present, the ambient temperature and in certain conditions, on the substrate at which the forces were measured. It is important to realize that it is not just hydration interaction that contribute to this force component. Other short-range interactions (most importantly the van der Waals interactions) will also play their part and, as I have shown in Chapter 2, it is challenging to disentangle such forces from the overall monotonic component. I have studied the influences of the uncertainties when calculating the van der Waals force between an AFM tip and substrate, and learned that describing the probe in detail is crucial: commonly, the tip is approximated as a solid sphere or as a flat plate which is described by a radius, but I have shown that, when dealing with nanometer-scale interactions, it is important to take the real shape of the tip into account. Since we have TEM images of our probes, we are in a good position to more accurately calculate the van der Waals force, and have shown that the uncertainties that remains, are not very significant since the sign of the forces do not vary within these uncertainties. Note, however, that we are applying a continuum interaction interpretation of the van der Waals force in a regime that we know had discrete properties; this is an unfortunate blind-spot that we cannot account for at the current level of understanding of short-range interactions. If it is be assumed that this unknown uncertainty does not significantly alter the known uncertainties, I can conclude that it is unlikely that the attractive monotonic interactions arise due to contributions from the van der Waals force: after subtracting van der

Waals force, the force remains attractive. Therefore, the short-range forces between hydrophilic surfaces in aqueous solutions can be attractive, at least in part due to hydration interactions. This is important to realize when studying colloidal and (bio-)molecular interactions between bodies in aqueous solutions.

It was not clear if and how the oscillatory and the monotonic contribution to the hydration force are correlated. This work indicates that there are not, since the oscillatory contribution is really robust in the forces that we have measured, while the monotonic contribution changes by varying environmental conditions. Based on this, it also seems that there are no differences in origin of the hydration forces at different surfaces, at least in our experiments at mica and silica, and that, when comparing these substrates, the hydration force is barely affected by the type of surface at which the forces are measured. The packing or layering of water molecules at the surface, at mica and silica, results in the oscillatory contribution to the force, while the monotonic contribution might show variations depending on the environmental condition.

7.2 Outlook

To understand the origin of the attractive force that was found between hydrophilic surfaces in the first nanometers from the mica surface, one needs to develop a theoretical model that can describe these short-range forces, which is challenging since continuum theories do not apply in this discrete regime. MD simulation where the AFM tip is taken into account are valuable¹, since it can bridge force data to atomistic solvation structures. However, as of now, the monotonic hydration force has not been addressed in these studies, likely due to the fact that the AFM tip is usually not taken into account. While, when one would study the interaction forces between the tip and surface using MD, it might shed light on its origin. In combination with experiments as performed in this thesis, one could look into the water molecule orientation, the density and learn if it does alter the sign of the interaction force. Additionally, by utilizing SFG experiments, one could study the orientation of water in the presence of specific salts. If we would be able to combine the knowledge of orientation of water molecules and water densities, we might learn why

and how these aspects translate to hydration interactions, and eventually how to control them.

It is argued that the hydration force is important in many systems ranging from proteins², to DNA³ and to colloidal systems⁴. We have learned a lot of the hydration forces in simple systems (mica and silica), however, as of yet we cannot directly correlate these finding to for example proteins or steric acid layers. In order to study how hydration contributes to these molecular interactions, it would be interesting to extend our knowledge on hydration forces between surfaces and chemically modified AFM tips. It is possible to grow single molecular chains on tips, such that molecule – surface interactions can be measured.⁵

3D hydration force mapping could eventually be applied to chemically heterogeneous surfaces as an analytical technique. It is already reported that the hydration structure is hard to observe in steps or edges.⁶ It would be interesting to map the hydration structure of particles that consist of two or more different facets. By analyzing the individual forces at specific, selected locations, one could study the influence of the surface chemistry on the oscillatory and monotonic contribution to the force. So, there are many more opportunities for AFM to add additional knowledge of our current understanding of hydration forces.

Additional experimental techniques should be used to bridge our knowledge of the solid-liquid interface to the forces that are measured in AFM. X-ray diffraction can resolve the structure of the solid-liquid interface.⁷ It would be interesting to be able to correlate the 3D hydration force to the structure found by diffraction techniques. This is of course challenging since the length scales probed are very different in size, but it would be interesting to see to what extent we can compare the finding in these techniques. Would it not be interesting if we could relate the location of adsorbed ions to the magnitude of the hydration force?

7.3 References

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We have arrived at the final part of the thesis, also known as the most read chapter. What comes to my mind when writing it is the following phrase:

‘In the sunset of dissolution, everything is illuminated by the aura of nostalgia, even the guillotine.’

This journey would have not been possible without the great people I am surrounded with.

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