Surface Forces Characterization of Polyelectrolyte Monolayers and Multilayers

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1 Introduction

Polyelectrolytes (PEs) remain among the least understood materials in soft matter, despite their widespread presence and use. One common use is in surface functionalization, where PEs adsorb with many weak bonds. Thus, they form durable coatings, and have been employed in a multitude of applications, such as wet and dry strength additives in flocculating or dispersing agents [Bolto and Gregory, 2007; Antonietti et al., 1994]. Often the surface coverage is known [van de Steeg et al., 1992; Fleer et al., 1993; Szilágyi et al., 2014; Butt and Kappl, 2010], but there is no clear relationship between surface coverage and conformation. Therefore, surface functionalization is empirically optimized. The adsorption conditions are varied, and the physical properties of the polymer film are determined.

The adsorption of neutral polymers is well understood. For polyelectrolytes, additionally, one needs to consider electrostatic interactions. Strong electrostatic forces in salt-free solutions with a large amplitude and long range are well understood, both theoretically [Holm et al., 2004; Netz and Joanny, 1999] and experimentally [Berndt et al., 1992; Lowack and Helm, 1998; Claesson and Ninham, 1992; Popa et al., 2010a; Kulcsár et al., 2005]. The adsorbed polyelectrolytes exhibit a flat conformation accompanied by surface charge overcompensation. However, in most practical cases, such as water purification [Rivas et al., 2003] or biological applications [Boudou et al., 2010; Dizge et al., 2018], PEs are dissolved in solutions with intermediate or high ionic strength. The electrostatic forces are then screened and are therefore weaker. Experimentally, one finds an increased PE coverage [Fleer et al., 1993; Szilágyi et al., 2014]. In these cases, the conformation of adsorbed PE monolayers on surfaces is known only for a few cases. There are some experiments which suggest instead surface coverage is accompanied by chains protruding into solution [Notley and Leong, 2010].

Polyelectrolyte multilayer (PEM) films are adsorbed on a substrate using the so-called layer-by-layer dipping method [Decher and Hong, 1991]. The adsorption process of the polyelectrolytes from water depends on the charge of the substrate and the PEs. By sequentially adsorbing polycations and polyanions onto a negatively charged substrate, the electrostatically connected polyelectrolyte multilayer
film is formed. After repeated adsorption, a strong self-assembled polyelectrolyte multilayer with a complex composition could be built [Schönhoff, 2003]. PEMs have been used in different biological applications such as drug delivery and biomedical implants. For example, antioxidant particles and drugs are coated with PEMs, which could be later irradiated to achieve targeted drug release [Hammond, 2012; Caruso et al., 2000; Bhalerao et al., 2014; Donath et al., 1998; Zhao and Liu, 2014]. Polyelectrolyte multilayers are also used to reduce the corrosion in stainless steel and aluminium [Farhat and Schlenoff, 2002; Shchukin et al., 2006; Dai et al., 2000].

To investigate the conformation of the polyelectrolytes adsorbed from different solutions, we use surface forces experiments. Previous force-distance experiments between identical surfaces covered with linear PEs adsorbed from 1 M NaCl showed that PEs adsorbed as pseudo-brushes onto oppositely charged surfaces, and the interaction of the pseudo-brushes was described by steric forces [Block and Helm, 2007] as predicted for neutral brushes [de Gennes, 1980; Alexander, 1977; de Gennes, 1987]. Polymer brushes refer to chains which are attached to a surface with a large anchoring density; the chains protrude into solution. On the approach of two surfaces covered with polyelectrolyte brushes, a repulsive steric force is observed when the outer segments of the polymer chains overlap [Israelachvili, 2011].

In polyelectrolyte brushes, all counter-ions are incorporated into the brush leading to brush neutralization [Liberelle and Giasson, 2008; Zhulina et al., 1995; Ahrens et al., 1998; Balastre et al., 2002; Mei and Ballauff, 2005]. Polyelectrolyte brushes swell and shrink depending on the concentration of monovalent ions \( I_{NaCl} \) in the measuring solution. The brush thickness \( L \) is proportional to \( (I_{NaCl} s^2)^{-\alpha} \) with scaling exponent \( \alpha \approx -1/3 \). Here, \( s^{-2} \) is the average grafting density. While \( L \) determines the range of the steric force, its amplitude is proportional to \( s^{-3} \). The pronounced swelling and shrinking are due to a balance between entropic and electrostatic forces. The former oppose stretching. However, electrostatic forces stretch the brush since an excess of counterions is incorporated into the brush to compensate the charge of the chains. The additional counterions in the brush cause an osmotic pressure. Increasing the salt concentration \( I_{NaCl} \) in the measuring solution decreases the imbalance between the counterion concentration in the brush and in the subphase. Therefore, the osmotic pressure within the brush is reduced and the brush shrinks (i.e., \( L \) decreases).

The theory of interaction between two neutral polymer brushes was successfully applied to describe the interaction of surfaces covered with PE brushes. Surface forces experiments successfully used these theories both for swollen and shrunken PE brushes [Liberelle and Giasson, 2008; Balastre et al., 2002]. Furthermore, PE
brushes attracted some attention in recent years because the increased ion concentration in the brush compared to the solution facilitates or hinders reactions [Lu and Ballauff, 2016; Wittemann et al., 2003], also the adsorption of oppositely or equally charged nano-objects is affected [Ballauff, 2007].

Concerning different polyelectrolytes adsorbed from high concentration of monovalent ions, the observed steric forces were all long-ranged [Block and Helm, 2007], and could be described as pseudo-brushes. When the salt concentration in the measuring solution was changed, the pseudo-brushes showed the scaling of a PE brush. The thickness of the pseudo-brush was found to depend on the kind of PE used and its molecular weight [Block and Helm, 2007, 2009].

Polyelectrolytes adsorbed onto a surface are not chemically bound, just physisorbed. Thus, their binding to the substrate is weaker, and one might expect reversible binding upon increase or decrease of the NaCl concentration of the measuring solution. Nevertheless, for PEs adsorbed from 1 M NaCl solutions onto an oppositely charged surface, it was found that the brush thickness scales like a salted brush [Block and Helm, 2007, 2008]. On decrease of the salt concentration the average distance between grafting points, $s$, increased by less than 50%. This finding suggests that stretching of the chains is accompanied by only minor structural rearrangements of the PE layer. This conclusion is supported by the reversible stretching and swelling of the pseudo-brushes [Block and Helm, 2007, 2008].

The polyelectrolyte multilayer has been used in many interfaces for bio-materials. Cell adhesion to the substrate is one of the most difficult problems in surface science nowadays. The PEM can introduce a very well-defined surface topology for cell adhesion. It is known that the [PSS / PDADMA] polyelectrolyte multilayer, until the number of layer pairs 12 (parabolic growth regime), provides an adhesive substrate for cells. Increasing the number of layer pairs (linear growth regime) causes poor cell adhesion [Arias et al., 2016]. PDADMA/PSS multilayers with PSS as a top layer adsorbed very few negative proteins like albumin [Dizge et al., 2018; Salloum and Schlenoff, 2004]. However, PDADMA terminated multilayer films behave as veritable sponges during protein adsorption [Salloum and Schlenoff, 2004]. Therefore, we want to investigate the top layer (PSS and PDADMA) of PEM films and how the structure of the physisorbed top layer is affected by increasing the number of layer pairs and the addition or removal of salt to the surrounding solution. We hope thus a better understanding of the surface forces ruling the adsorption of PEs can be achieved. It is possible in this way to gain more insight into the surface charge, the surface potential, the grafting density and the thickness of pseudo-brush of a PE layer as well as the top layer conformation of a PEM film.
Also, it is possible that the polyelectrolytes are adsorbed flatly. Then, electrostatic forces as predicted by the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory describe the interaction of the surfaces [Derjaguin and Landau, 1941; Verwey and Nes, 1948].

1.1 Motivation of PDADMA/PSS multilayers

The aim of this part of the thesis is to investigate the top layer (PSS and PDADMA) conformation of polyelectrolyte multilayer films and how the structure of the physically sorbed top layer is affected by increasing the number of layer pairs and the salt concentration in the surrounding solution. This allows for a better understanding of the surface forces ruling the adsorption of polyelectrolytes onto oppositely charged surfaces. In this way, it might be possible to gain more insight into the surface charge, the surface potential, the grafting density as well as the conformation of the PEs at the surface: flat or pseudo-brushes. With help from atomic force microscopy (AFM) and the colloidal probe technique (CPT) as the high-resolution technique, we were able to perform such an investigation.

PDADMA/PSS multilayers are explored because they are well characterized PEMs with lots of polymers with low polydispersity index (PDI). Polydiallyldimethylammonium (PDADMA) has a smaller linear charge density than polystyrene sulfonate (PSS). For this system, two different growth regimes are known: (1) “parabolic” [Nestler et al., 2013; Ghostine et al., 2013] which contains the same amount of positive and negative monomers and (2) “linear” which is characterized by a larger amount of positive monomers than of negative monomers. For charge neutrality, these PEMs contain an excess of monovalent negative ions. Upon the increase of the ion concentration in the surrounding medium beyond the preparation concentration, some ionic monomer-monomer bonds are replaced by ion-monomer bonds. This is shown by neutron reflectivity which demonstrates an increased mobility of chains within the multilayer film in higher salt concentrations [Soltwedel et al., 2010].

1.2 Motivation for PEI monolayers

In solution, the interactions between divalent or trivalent metal ions and water/soluble PEs have attracted interest due to their intrinsic properties as well as their potential applications, such as water purification, or binding to biocompatible polymers [Liberelle and Giasson, 2008; Juang and Chen, 1996; Lim et al., 2013]. The cases
when a weakly charged PE and the metal ion have the same charge are especially of interest; the addition of divalent ions with opposite charge often causes the PE to collapse and precipitate. Oppositely charged metal chelates with their large diameter remain in solution together with the PEs. Actually, in water purification, the retention rate of metal ions is larger when chelates are used [Juang and Chen, 1996]. Biological applications address other questions: it is a concern that iron and gadolinium dissolved in aqueous solution are toxic. However, iron is essential for the body. Gadolinium is used as magnetic markers in MRT. Therefore, in biology and medical applications, these metal ions are never dissolved in solution, but always bound to other molecules, often chelating agents [Lim et al., 2013; Manoguerra et al., 2005].

Therefore, we also want to investigate a branched PE adsorbed from solutions containing divalent ions of the same charge. We chose branched polyethylenimine (PEI) as the polycation and Fe$^{2+}$ as a divalent ion. Similar to hemoglobin or ferritin, PEI interacts with Fe$^{2+}$ ions via cooperative bonds. These cooperative bonds stabilize a coiled conformation of PEI [Zhou et al., 1994; Zhu et al., 2006]. To explore the effect of a large oppositely charged divalent ion on PEI, Fe$^{2+}$ was complexed with EDTA. The multivalent anion EDTA stabilizes the coiled conformation of PEI by electrostatic bonds [Juang and Chen, 1996]. The conformation of adsorbed PEI with iron salts or iron chelates in the adsorption solution is also explored.

PEI layers adsorbed onto oppositely charged surfaces were characterized with X-ray reflectivity when the adsorption solution contained either FeSO$_4$ or EDTA chelates (FeSO$_4$ with an excess of EDTA) [Gröning et al., 2016]. Compared to a flat PEI layer adsorbed from salt-free water, the thickness of the PEI layer was increased by a factor of 3-4 when FeSO$_4$ were in the solution. As expected, the adsorbed PEI layer contained iron. With iron chelate in the solution, the thickness of the adsorbed PEI layer and its surface coverage increased even further, indicating that the PEI layer contained electrostatically bound iron chelates. It was concluded that in solutions containing iron ions or iron chelates the branched polyelectrolyte PEI is in a coiled conformation, and adsorbs in this coiled conformation. However, different molecular forces stabilize the coiled conformation: bi-directional cooperative bonds, if only iron ions are present, and directional electrostatic bonds if the solution contains iron chelates.

To probe the surface functionalization with PEI adsorbed from different solutions, gold nanoparticles are adsorbed onto the PEI-functionalized surfaces [Schmitt et al., 1999; Ghosh and Pal, 2007], and their number density is determined. AuNPs are especially suited to investigate surface functionalization: one can not only deter-
mine the maximum number density with X-ray reflectivity and AFM, and due to
their distinct optical properties one can recognize aggregation easily. Briefly, neg-
avatively charged AuNPs adsorb onto positively charged surfaces due to electrostatic
attraction [Schmitt et al., 1999; Ghosh and Pal, 2007]. Adsorbed onto the surface,
they repel each other within the surface plane electrostatically. This in-plane elec-
 trostatic repulsion limits the maximum surface coverage. If the AuNPs touch each
other due to bridging forces caused by PE chains protruding into solution, their
optical properties change; isolated AuNPs exhibit a localized surface plasmon res-
onance which leads to a distinct absorption peak, while aggregated AuNPs show a
second peak.

1.3 Structure of the thesis

This thesis is organized as follows:

Chapters 2 and 3 introduce the important properties of polymers from the physical
point of view. The basic information about different types of the conformation of
linear PE is briefly described. The most popular models to describe the confor-
mation are discussed. Also, the charged surfaces and their electrostatic interaction
forces are included. The Derjaguin approximation and DLVO theory are briefly
explained. Moreover, some theoretical information about steric forces of adsorbed
polymers is also briefly introduced. In chapter 4, I will present the most impor-
tant experimental fundamentals and setups used in this thesis. An overview of
AFM, diffusion, UV-Vis spectroscopy, and X-ray reflectivity as important setups
for the measurements and data analysis will be provided. Chapter 5 describes the
materials, sample preparation, and data analysis used to achieve the different force-
distance measurements. The procedure for sample preparation is also described.
AFM sample preparation is described in detail: colloidal probe attachment to the
cantilever and measurement of the cantilever spring constant. Finally, theoretical
models used for the evaluation of force-distance curves are presented.

Chapter 6 provides information about surface forces between the PEM top layers
with different terminating layers as a function of the number of layer pairs and ionic
strength. The effect of increasing the number of layer pairs on the surface charge
and surface potential of the PSS terminated surface is described and discussed.
The effect of increasing the number of layer pairs on the PDADMA terminated
surface is also provided. The behavior of both terminating layers is intensively
tested at different ionic strengths. Chapter 7 provides information about surface
forces between PEI layers physisorbed in the presence of iron ions, and iron chelate
1.3 Structure of the thesis

and pure water and the deduced surface forces including theoretical analysis. The surface conformation of three physisorbed PEI is studied. The influence of different PEI conformation on the adsorption of gold nanoparticles is investigated. Chapter 9 provides all supporting information needed for force analysis, control experiments, and fitting parameters.
2 Theoretical Background

Polymers are macromolecules which consist of small repetitive units called monomers. The monomers are connected by chemical bonds. The number of monomer units or segments per polymer molecule is the degree of polymerization \( N_{pol} = M_w/M_0 \) where \( M_w \) is the molecular weight of the polymer molecule and \( M_0 \) is the molecular weight of the monomer. One monomer can be from the size of an angstrom to a few nanometers [Flory, 1953]. \( N_{pol} \) is typically between \( 10^2 \) and \( 10^{11} \). The length of the fully extended polymer chain is defined as contour length \( (L_c = N_{pol}l) \) and is usually between 10 nm and 10 m, where \( l \) is the monomer length. A single human chromosome consists of a DNA molecule that has a contour length of almost 5 cm. These connected monomers can take many forms such as straight chains, branched chains or form complicated shapes like proteins [Fleer et al., 1993]. The main body or the backbone of the polymer contains a variety of side groups which can be atoms or functional groups with free bonds. These functional groups such as alkyl, carboxylic acid, and ester groups, etc., define the chemical properties of polymers. This introduces different types of polymers. If a polymer consists of identical connected monomers, it is defined as a homopolymer. Heteropolymers are formed of several different monomer units, e.g., DNA. Block copolymers are built from a number of blocks each being a homopolymer or heteropolymer by itself (Fig. 2.1). Dissociation of monomers in water leads to charged polymers such as the well-known PEs [Armstrong and Strauss, 1969]. One of the most important properties of PEs is their water solubility. PEs could also be considered as flexible or semi-flexible chains. A flexible chain does not cost energy to bend them, therefore it is coiled; however, the rigid semi-flexible chain is the more real scenario. For PEs, the charged groups play an important role in the stiffness of the chain [Netz and Andelman, 2003].
2.1 Conformation of Linear Chains

Different models have been developed to introduce a theoretical description of the single polymer molecules, for which mostly classical partition theories can be given. Some of these models are the freely-jointed chain (FJC), the freely rotating chain (FRC), the worm-like chain (WLC) and the excluded volume models.

2.1.1 Freely jointed chain (FJC)

It is also the so-called random-flight model, flexible or ideal chain. This model assumes the chain consists of $N + 1$ monomers which are connected by $N$ bonds. Every monomer is represented by a vector which has a fixed length $|r_j| = a$ (equal to the Kuhn length), with $j = 1, ..., N_{pol}$. The segments are able to rotate around each other freely in any direction, i.e., the direction of a segment is uncorrelated with adjacent segments (Fig. 2.2). In the absence of any net forces acting on the monomers and by using the random walk assumption, the mean square end-to-end distance $R_0$ of the chain is calculated as
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\[ R_0 = \langle R^2 \rangle = a^2 N_{pol} = L_c a \]  \quad (2.1)

\( R_0 \) is an average length to represent all over the chain dimension. By assuming that the polymer chain is occupying a sphere, the radius of this sphere in space is called the radius of gyration \( R_g \). The radius of gyration which is the root mean square distance between the monomers and the chain center of mass is given as

\[ R_g = R_0 / \sqrt{6} \]  \quad (2.2)

This is the effective size of the coil (blob). In this model, the segments lose the angular correlation after traveling one Kuhn length \( a \), so that the real size of the chain is very different than \( R_g \). This means that Eq. 2.2 is only valid as long as the solvent is ideal for the polymer which means there is no attraction and repulsion or excluded volume between the monomers. For a non-ideal solvent, which is the real case, the effective size of the coil can be larger (swelling effect) or smaller (collapse effect) than \( R_g \) [Israelachvili, 2011].

### 2.1.2 Freely rotating chain (FRC)

The polymer backbone bonds of length \( b \) cause a torsional rotation at fixed bond angle \( \theta \). This leads to the so-called freely rotating chain (FRC) conformation (cf. Fig. 2.2). Here, contrary to the FJC model, the correlation between two neighboring bond vectors is not zero but is \( \langle r_j, r_{j+1} \rangle = b^2 \cos \theta \). Moreover, correlations are transferred through the backbone to further neighbors, so the bond-vector correlation function is [Grosberg and Khokhlov, 1994]:

\[ \langle r_j, r_k \rangle = b^2 (\cos \theta)^{|j-k|} \]

The mean-squared end-to-end radius for long chains \((N \to \infty)\) is defined as [Grosberg and Khokhlov, 1994]

\[ R_0 \approx N_{pol} b^2 \frac{1 + \cos \theta}{1 - \cos \theta} \]

the FRC contour length is \( L_c = N b \cos (\theta/2) \). Using the scaling relation \( R^2 = aL \) to form the FJC model, the Kuhn length \( a \), for the FRC model is
2.1 Conformation of Linear Chains

\[ a = b \frac{1 + \cos \theta}{\cos(\theta/2)(1 - \cos \theta)} \]

For a saturated carbon backbone with bond angle \( \theta \approx 70^\circ \), the Kuhn length \( a \approx 2.5b \). If the monomer size or bond length is \( b \approx 0.15 \text{ nm} \), then one obtains a Kuhn length of \( a \approx 0.38 \text{ nm} \) [Netz and Andelman, 2003].

Figure 2.2: (left) The wormlike chain (WLC) model as a continuous chain has an angular correlation and is described by persistence length \( L_p \). (middle) The free rotating chain (FRC) model with a fixed bond angle \( \theta \). (right) The free jointed chain (FJC) model which describes the chain as a discrete sequence of N steps with a constant step size \( a \). From [Netz and Andelman, 2003; Block, 2010].

2.1.3 The Worm-Like Chain Model

The WLC model is used to describe the stretching behavior of “stiffer” polymer molecules and it provides more relevant results than, for example, the FJC model [Kratky and Porod, 1949; Porod, 1949]. The random walk in FJC model is replaced by a continuous flexible rod in terms of a bending modulus, or a persistence length \( L_p \) which describes the decay in correlation to tangent vectors (cf. Fig. 2.2), or for an infinitely long chain, it is the average sum of the projections of all bonds \( j \geq i \) on the bond \( i \) [Flory, 1969]:

\[ < \vec{e}_i(r_1), \vec{e}_i(r_2) > = e^{-|\vec{r}_1 - \vec{r}_2|/L_p} \]

The persistence length is also expressed by the bending stiffness \( EI \) as [Baumann et al., 1997]

\[ L_p = \frac{EI}{k_B T}, \text{ and } I = \frac{\pi r^4}{4} \text{ for a rigid, and uniform rod} \]

\( E \) is Young’s modulus, and \( r \) is the rod radius.
The mean square end-to-end distance $R$ for WLC can be calculated as:

$$R^2 = 2L_p^2 \left( \frac{L_c}{L_p} - 1 + e^{-L_c/L_p} \right)$$  \hspace{1cm} (2.3)$$

And the radius of gyration is given by [Benoit and Doty, 1953]

$$R_g^2 = \frac{L_p}{3L_c^2} \left( L_c^3 - 3L_cL_p + 6L_cL_p^2 - 6L_p^3 \left( 1 - e^{-L_c/L_p} \right) \right)$$  \hspace{1cm} (2.4)$$

This has two limiting cases, the first is for $L_p \ll L_c$ which simplifies to the freely-jointed or $L_p \approx L_c$ and Eq. 2.3, Eq. 2.4 are rewritten as

$$R^2 = 2L_cL_p \quad \text{and} \quad R_g^2 = \frac{1}{3}L_cL_p$$  \hspace{1cm} (2.5)$$

In the second, at large value of $L_p$, the polymer behaves like a stiff rod and

$$R = L_c \quad \text{and} \quad R_g = L_c/\sqrt{12}$$  \hspace{1cm} (2.6)$$

In this model, the polyelectrolytes expect to have higher bending rigidity compared to uncharged polymers. Therefore, the WLC model is more realistic to describe polyelectrolytes than other models.

### 2.1.4 Excluded volume model [Israelachvili, 2011]

Flory [Flory, 1969] addressed a more realistic theory to explain the excluded volume of a simple linear chain in a solution. He introduced Flory radius, $R_F = \alpha R_g$ where $\alpha$ is the intramolecular expansion factor and $(\alpha = 1)$ describes the ideal solvent. In a good solvent, the segments repel each other $(\alpha > 1)$ and the excluded volume of the chain is larger than that of an ideal chain. This is a swelling effect and the chain becomes more extended. In contrast, in a poor solvent, the attractive interaction dominates $(\alpha < 1)$, and the chain shrinks giving a negative excluded volume. For perturbed chains, the excluded volume points to the one part of a long chain that can not exist in the space that is by now occupied by another part of the same chain [Hill, 1986]. In this case, the characteristic size of an excluded volume chain with $N_{pol}$ monomers is proportional to $N_{pol}^{3/5}$. The polymer chain searches for equilibrium by minimizing the free energy. This happens by the repulsive interaction between the monomers (osmotic forces). Therefore, the monomers can avoid each other. As a result, the loss in entropic forces caused by chain expansion is balanced by osmotic
forces. This assumption is used to calculate a general scaling of the perturbed average end-to-end distance $R$ [De Gennes, 1979; Cardy, 1996]

$$R \sim N_{pol}^{3/(d+2)}$$

where $d$ is the allowed dimension in space for the chain to expand. For repulsive interaction between the monomers, the scaling exponent is larger than 0.5, and it is found for ideal chains in theta solvent. Thus the chain is protruded by extending in the solution. By taking only the excluded volume of the chain into account, this prevents the shrinking of the chain by the monomer–monomer interaction, and one obtains [Netz and Andelman, 2003]

$$R \sim N_{pol}^{1/3}$$

### 2.2 Polyelectrolyte chains [Netz and Andelman, 2003]

PEs are weakly or strongly charged. The effective charge of each monomer is controlled by the ionic strength and pH of the solution. The electrostatic interaction energy between two point charges of valency $Z_1$, $Z_2$ separated by distance $r$ in salt-free solution can be written as

$$W(r) = \frac{Z_1 Z_2 l_B}{r}$$

where $l_B$ is the Bjerrum length, which is defined as

$$l_B = \frac{e^2}{4\pi\varepsilon\varepsilon_0 k_B T}$$

where $\varepsilon$ is the dielectric constant of the medium, $\varepsilon_0$ is the vacuum dielectric constant and $e$ is the elementary charge. At this Bjerrum distance, the coulombic interaction between two unit charges is equal to the thermal energy $k_B T$ ($T = 300$ k) and $l_B \approx 0.71$ nm at room temperature in water. In most cases, mobile ions dissolve in aqueous solution. Different ions or counterions are attracted by the charged monomers leading to a screening of the coulombic interaction given by:

$$W(r) = \frac{Z_1 Z_2 l_B}{r} e^{-\kappa r}$$
For an isolated PEs chain, the electrostatic repulsion between monomers increases the effective persistence length $L_p$. The adsorption behavior of the PEs in a solution will be changed. At weak electrostatic energy and if the contour length $L_c$ is long enough ($L_c \gg L_p$), an unperturbed polymer coil will be formed with a radius $R$. Using Eq. 2.4, $R^2 \approx 2L_pL_c$. If the electrostatic is strong enough, the PEs chain will swell. For PE with line charge density $\tau$, the total charge $Z = \tau L_c$. The electrostatic energy for a spherically shaped PE coil is

\[ W_{el} = l_B \tau^2 L_c^{3/2} L_p^{-1/2} \]

The chain length $L_{el}$ at which the electrostatic self-energy is in the order of $k_B T$, i.e., $W_{el} \approx 1$, is then [Netz and Andelman, 2003]

\[ L_{el} = L_p (l_B L_p \tau^2)^{-2/3} \]

This $L_{el}$ introduces the electrostatic blob size or the electrostatic polymer length. If the electrostatic energy between two monomers with length $L_p$ is less than the thermal energy, then it is not enough to align the chain against the Brownian motions and the chain will be crumpled.

\[ L_{el} > L_p \text{ and } \tau \sqrt{l_B L_p} < 1 \]

In contrast, if the electrostatic monomer–monomer repulsion is significant on length scales similar to the persistence length, the chain will be stretched.

\[ L_{el} < L_p \text{ and } \tau \sqrt{l_B L_p} > 1 \]
2.2 Polyelectrolyte chains [Netz and Andelman, 2003]

Figure 2.3: (left) Low electrostatic energy between the segments and these monomers are crumpled by the thermal energy and forming blobs $L_{el} > L_p$. (right) Electrostatic monomer–monomer repulsion is strong enough to be on length scales similar to the persistence length, the chain will be stretched $L_{el} < L_p$, where $L_{el}$ introduces the electrostatic blob size and $L_p$ is the bare persistence length [Block, 2010].

In this case, the conformation of the chain is characterized by an effective persistence length $L_{p,eff}$, and $L_{p,eff} > L_p$. Although the contour length is larger than the bare persistence length $L_p$, the polyelectrolyte remains locally stiff and the effective persistence length is defined as

$$L_{p,eff} \simeq L_p + L_{el,p},$$

where $L_{el,p}$ is the electrostatic contribution to the effective persistence length, and was calculated by Odijk, Skolnick, and Fixman [Odijk, 1977; Skolnick and Fixman, 1977; Odijk and Houwaart, 1978]

$$L_{el,p} = \frac{l_B \tau^2}{4\kappa}$$
3 Charged surfaces and interaction forces

In this chapter, the fundamental information related to interaction forces between charged surfaces will be summarized. We introduce the important equations, models, and approximations related to electrostatic, steric and dispersion (van der Waals) forces used in the discussion. The most important information that related to our materials of interest, neutral and charged polymers, will be described, here.

3.1 Derjaguin Approximation [Israelachvili, 1991]

The interaction forces between macroscopic bodies are experimentally easier to measure than the interaction potential. Derjaguin introduced an approximation valid if the distance \( D \) between two surfaces of spheres is much smaller than their radius of curvature. The force acting between the two surfaces \( F(D) \) can be described by the energy per unit area \( W(D) \) of the corresponding flat surface [Derjaguin, 1934; Israelachvili, 1991]. This Derjaguin approximation is mainly suitable for CPT in the AFM experiment (cf. Fig. 3.1), as it can be used in the case of two interacting spheres or a sphere interacting with a flat surface. The interaction energy between two spheres with radius \( R_1 \) and \( R_2 \) respectively is

\[
F(D) = 2\pi \frac{R_1 R_2}{R_1 + R_2} \cdot W(D) \tag{3.1}
\]

In the case of a sphere \((R_1 = R)\) interacting with a flat surface (radius, \( R_2 = \infty \)), it is convenient to normalize force in CPT to \( R \),

\[
F(D) = 2\pi R \cdot W(D) \tag{3.2}
\]

3.2 DLVO Theory [Israelachvili, 2011]

The individual consideration of the electrostatic potential due to the so-called electric double layer of counterions interaction between two surfaces does not describe all experiments. Derjaguin, Landau [Derjaguin and Landau, 1941], Verwey, and Overbeek [Verwey and Nes, 1948] extended the theory of Coulomb force to include the van der Waals (vdW) interaction. The electrostatic part of the DLVO theory is figured by the mean field estimation under the condition that the potential energy of an elementary charge on the surface is much smaller than the thermal energy ($k_B T$). By approaching two surfaces to each other, the overlap between the electrical double layers rises and Coulomb repulsion increases. Additionally, the dispersion (or vdW) attraction increases as the two surfaces get closer. Therefore it is likely, to sum up the energies arising from the electrostatic interaction and the dispersion individually and the sum of them gives an interaction energy:

$$W(D) = W_{vdW}(D) + W_{dl}(D)$$  \hspace{1cm} (3.3)$$

where $W_{dl}(D)$ is the interaction energy due to electric double layer and $W(D)_{vdW}$ is the attractive interaction energy as a result of van der Waals interaction.

Van der Waals force always acts and it is a consequence of interactions of the fluctuating electrical dipoles of atoms and molecules. Different than the electrostatic interaction, the vdW potential is largely not sensitive to variations in salt concentrat-
tion and pH. Furthermore, the vdW attraction must always exceed the double-layer repulsion at small enough distances. This vdW interaction can be described as:

\[
W_{\text{vdW}}(D) = -\frac{H}{12\pi D^2}
\]  

(3.4)

H is the Hamaker constant and it is in most situations positive. Therefore the vdW force is attractive. As vdW force is a short-range interaction, it is often neglected. Electrostatic interactions as long-range forces can be more important for charged surfaces.

3.2.1 The electric double layer at a charged interface

The majority of immersed surfaces are charged in aqueous solutions. Different functional surface groups ionize or dissociate in water and cause a surface charge. Depending on these chemical groups, the surface charge can be positive or negative. Silicon and silicon dioxide, for instance, have negative surface charges because of dissociation of hydroxyl groups in the water leading to form silanol groups [Papirer, 2000]:

\[
R - \text{SiOH} \rightleftharpoons R - \text{SiO}^- + H^+
\]

With the same charge mechanism, at low pH value, amino groups are protonated and the positive charges are increased [Butt et al., 2006; Pericet-Camara, 2006]. The terminated surface with protonated amino groups is less negative by producing amino-silanes:

\[-NH_2 + H^+ \rightleftharpoons -NH_3^+
\]

whilst, the dissociation of carboxylic groups at high pH form negative charges and increase the surface negativity:

\[-\text{COOH} \rightleftharpoons -\text{COO}^- + H^+
\]

The charging surface process could also happen by adsorbing ions (counter- or co-ions) from the solution. The counter- or co-ions will be attracted or repelled by the charged surface. The counter-ions density increases because of attraction to the surface and simultaneously the co-ions density decreases due to the electrostatic repulsion (cf. Fig.3.2). Because of surface charges, a small electrical potential similar to the thermal energy \(k_B T\) is generated. The adsorbed counter-ions form
near to the surface the so-called Stern or Helmholtz layer. When the distance to the charged surface is increased, Coulomb attraction competes against the Brownian motion and a diffuse or Gouy-Chapman layer is formed. Effective charge reversal can also happen by adsorbing macro-ions like polyelectrolytes and surfactants.

Figure 3.2: Stern model introduces the distribution of co- (blue) and counter-ions (red) near to the charged surface in solution. The counterion density decreases with increase of the distance to the charged surface.

3.2.2 Nonlinear and Linear Poisson–Boltzmann Equation

For a charged planar surface with an ion density $\sigma_0$ at location $z = 0$, the profile of charges density could be shown as in (cf. Fig. 3.2) bottom. The chemical potential $\mu_i$ of anionic species $i$ dissociated in an equilibrium system is defined as:

$$\mu_i = W_i(z) + k_B T \log \rho_i(z) \to \rho_i(z) = \rho_{i,\infty} e^{-[W_i(z) - W_i(\infty)]/k_B T}$$  (3.5)
where \( \rho_i(z) \) is the number density of \( i \)-th species at any position \( z \). The potential energy of position of \( i \)-th species \( W_i(z) \) is described by the mean field theory (replace ion-ion interactions by an ion interaction with an effective potential) as \( W_i(z) = Z_i \cdot e \cdot \psi(z) \) where \( e \) is the elementary charge, \( Z_i \) is the valence of the ion and \( \psi(z) \) is the electrostatic potential. \( \rho_{i,\infty} \) is the bulk concentration of the \( i \)-th species. At an infinite distance to the surface, the potential energy \( W_i(\infty) \) can be set to zero. As equilibrium system, the chemical potential is uniform at any position \( z \) and classical Boltzmann distribution is applied for the number density of ions as follows:

\[
\rho_i(z) = \rho_{i,\infty} e^{-Z_i \cdot e \cdot \psi(z)/k_B T} \tag{3.6}
\]

Here, the electrostatic potential and net charge density must satisfy the Poisson equation:

\[
\frac{d^2 \psi(z)}{dz^2} = -\sum_i Z_i e \rho_i(z) \tag{3.7}
\]

\( \varepsilon_0 \) and \( \varepsilon \) are the dielectric constant in vacuum and solution respectively. Together with the Boltzmann distribution Eq.3.6, Eq.3.7 gives us the nonlinear Poisson-Boltzmann equation (PB):

\[
\frac{d^2 \psi(z)}{dz^2} = -\sum_i Z_i e \rho_i(z) \frac{1}{\varepsilon_0} e^{-Z_i e \psi(z) / k_B T} \tag{3.8}
\]

To solve PB equation as a non-linear differential equation of second order, it is necessary to have two boundary conditions. First one, \( \psi_0 = \psi(z = 0) \), by symmetry. The second condition, all ions in the medium equal and opposite to the charge on the surface because of electroneutrality. By integrating Eq.3.7, the surface charge density \( \sigma_0 \) (in Cm\(^{-2}\)) is given as

\[
\sigma_0 = -\int_0^\infty \sum_i Z_i \varepsilon_0 \rho_i(z) \, dz = -\varepsilon_0 \int_0^\infty \frac{d^2 \psi(z)}{dz^2} \, dz
\]
By differentiating Eq. 3.6 and using Poisson equation (Eq. 3.8) we get:

\[
\sum_i \frac{d\rho_i(z)}{dz} = \sum_i \rho_{i,\infty} e^{-\frac{Ze\psi(z)}{k_BT}} \cdot \left( -\frac{Ze}{k_BT} \right) \left( \frac{d\psi(z)}{dz} \right) = \frac{\varepsilon\varepsilon_0}{k_BT} \left( \frac{d\psi(z)}{dz} \right) \left( \frac{d^2\psi(z)}{dz^2} \right)
\]

Using the relations

\[
\frac{d}{dz} \left( \frac{d\psi}{dz} \right)^2 = 2 \left( \frac{d\psi}{dz} \right) \left( \frac{d^2\psi}{dz^2} \right)
\]

\[
\sum_i \frac{d\rho_i(z)}{dz} = \frac{\varepsilon\varepsilon_0}{2k_BT} \frac{d}{dz} \left( \frac{d\psi(z)}{dz} \right)^2
\]

\[
\sum_i \int_z^\infty \frac{d\rho_i(z)}{dz} dz = \sum_i \frac{\varepsilon\varepsilon_0}{2k_BT} \int_z^\infty \frac{d}{dz} \left( \frac{d\psi(z)}{dz} \right)^2 = \sum_i \rho_i(z) - \rho_{i,\infty}
\]

\[
\sum_i \rho_i(z) - \rho_{i,\infty} = \frac{\varepsilon\varepsilon_0}{2k_BT} \left( \frac{d\psi}{dz} \right)
\]

By using Eq. 3.9,

\[
\sum_i \rho_i(z = 0) - \rho_{i,\infty} = \frac{\varepsilon\varepsilon_0}{2k_BT} \cdot \left( \frac{d\psi(z = 0)}{dz} \right)^2 = \frac{\sigma_0^2}{2k_BT\varepsilon\varepsilon_0}
\]

This is the well known Grahame equation which could be rewritten for monovalent salt \((n : n)\) dissolved in aqueous solution as
\[\sigma_0^2 = 2k_B T \varepsilon_0 \left[ \sum_i \rho_i(z = 0) - \rho_i,\infty \right] = 2k_B T \varepsilon_0 \sum_i \rho_i,\infty \left[ e^{-\frac{Z_i \varepsilon_0}{k_B T}} - 1 \right] \] (3.12)

\[\Downarrow\]

\[\sigma_0^2 = 2k_B T \varepsilon_0 \sum_i \rho_i,\infty \left[ e^{-\frac{Z_i \varepsilon_0}{k_B T}} - 1 \right] = 2k_B T \varepsilon_0 \rho_\infty \left[ e^{-\frac{Z_i \varepsilon_0}{k_B T}} + e^{\frac{Z_i \varepsilon_0}{k_B T}} - 2 \right] \]

\[\Downarrow\]

\[\sigma_0^2 = 2k_B T \varepsilon_0 \rho_\infty \left[ e^{-\frac{Z_i \varepsilon_0}{k_B T}} + e^{\frac{Z_i \varepsilon_0}{k_B T}} \right]^2 = 2k_B T \varepsilon_0 \rho_\infty \left[ 2 \sinh \left( \frac{Z \varepsilon_0}{2k_B T} \right) \right]^2 \]

\[\Downarrow\]

\[\sigma_0^2 = 8k_B T \varepsilon_0 \rho_\infty \sinh^2 \left( \frac{Z \varepsilon_0}{2k_B T} \right) \]

\[\Leftrightarrow \psi_0 = \frac{2k_B T}{Ze} \asinh \left( \frac{\sigma_0}{\sqrt{8k_B T \varepsilon_0 \rho_\infty}} \right) \] (3.13)

where \( \rho_\infty \) is the electrolyte concentration in the bulk at \( z = \infty \). In case of using NaCl as electrolyte one can write charge density \( \sigma_0 \) in terms of surface potential \( \psi_0 \) with taking into account that \([\text{Na}^+]_0 = [\text{Cl}^-] \). For two surfaces separated by infinite distance or an isolated surface, Grahame equation can be summarized in the expression

\[\sigma_0 = \sqrt{8\varepsilon_0 k_B T \cdot \sinh \left( \frac{e \psi_0}{2k_B T} \right)} \sqrt{I_{\text{NaCl}}} \]

where \( I_{\text{NaCl}} \) is the ionic strength in Mol. The electrostatic potential can also define as

\[\frac{d\psi(z)}{dz} = \frac{\sigma_0}{\varepsilon_0} = \sqrt{\frac{8k_B T \rho_\infty}{\varepsilon_0}} \cdot \sinh \left( \frac{e \psi_0}{2k_B T} \right) \]

By integrating using \( \int \text{csch} z \, dz = \log \tanh(z/2) \), the electrostatic potential \( \psi(z) \) is given by

\[\psi(z) = \frac{2k_B T}{Ze} \log \left[ 1 + \frac{\gamma e^{-\kappa z}}{1 - \gamma e^{-\kappa z}} \right] \text{ with } \gamma = \tanh \left( \frac{Z \varepsilon_0}{4k_B T} \right) \] (3.14)
for $z \gg \kappa^{-1}$ \hspace{1cm} \psi(z) = \frac{4k_BT}{Ze} e^{-\kappa z} \tag{3.15}

### 3.2.3 Debye-Hückel approximation

It is a simple approximation to describe the electrolyte solution by bringing Poisson–Boltzmann equation in a linear form. At small surface potentials $\left|\frac{Z_i e \psi(z)}{k_B T}\right| < 1$, a Taylor expansion can be done. It is known as Debye-Hückel approximation,

$$\exp\left(-\frac{Z_i e \psi(z)}{k_B T}\right) = (1 - \frac{Z_i e \psi(z)}{k_B T} + \frac{\left[\frac{Z_i e \psi(z)}{k_B T}\right]^2}{2!} - ...) \approx 1 - \frac{Z_i e \psi(z)}{k_B T}$$

With using this approximation in Eq.3.8 we obtain:

$$\frac{d^2 \psi(z)}{dz^2} = -\sum_i Z_i e \rho_i,\infty \left(1 - \frac{Z_i e \psi(z)}{k_B T}\right)$$

which leads to the linearized version of Eq.3.8 or Debye-Hückel theory. In the bulk solution, the electroneutrality condition leads to $\sum_i \frac{Z_i e \rho_i,\infty}{\varepsilon \varepsilon_0} = 0$ and we obtain from Eq.3.16,

$$\frac{d^2 \psi_{DH}(z)}{dz^2} = \kappa^2 \psi_{DH}(z) \tag{3.17}$$

The solution of Eq.3.17 as an exponential approach,

$$\psi_{DH}(z) = \psi_{DH,0} e^{-\kappa z} \tag{3.18}$$

Using this approximation, one can write Eq.3.13 for $\sigma_0$ in terms of surface potential $\psi_0$ as

$$\sigma_{DH,0}^2 = 8k_B T \varepsilon \varepsilon_0 \rho_\infty \left(\frac{Z e \psi_{DH,0}}{2k_B T}\right) \Leftrightarrow \psi_{DH,0} = \frac{2k_B T}{Z e} \left(\frac{\sigma_{DH,0}}{\sqrt{8k_B T \varepsilon \varepsilon_0 \rho_\infty}}\right) \tag{3.19}$$

By definition of Debye-Hückel parameter $\kappa$ as,

$$\kappa^2 = \sum_i \frac{(Z_i e)^2 \rho_i,\infty}{\varepsilon \varepsilon_0 k_B T}$$

$$\kappa^{-1} = \sqrt{\frac{\varepsilon \varepsilon_0 k_B T}{(Z_i e)^2 \rho_i,\infty}} \tag{3.20}$$
The so-called Debye length $\kappa^{-1}$ corresponds to the fundamental length scale of the electrostatic double layer where the electrical potential is reduced by a factor $1/e$. If we consider 1:1 electrolytes ($Z = 1$) (e.g., NaCl) at $25^\circ$ C the Debye length in water is

$$
\kappa^{-1} = \frac{\varepsilon_0 k_B T}{(Z e)^2 \rho_i \infty} = \frac{0.304 \text{ nm}}{\sqrt{I_{NaCl}}}
$$

where $I_{NaCl}$ is the ionic strength of NaCl in Mol. From Eq. 3.15 and Eq. 3.18, we can deduce that the electrostatic potential $\psi(z)$ of a surface will decay by 63% by increasing the distance to the surface by $\kappa^{-1}$. This leads to a strong screening of the electrostatic potential. The mean field approach which includes the electrostatic interaction is also valid for most monovalent salts. However, many effects are being neglected as hydration forces [Block, 2010]. Further, taking the effective electrostatic potential ignores the finite size of the ions and solvent molecules. Solvent molecule size could be in the same order of Debye length, especially at a high salt counterion which gives a wrong estimation of counterion density.

### 3.2.4 Electrostatic Forces between two planar surfaces

![Diagram showing electrostatic forces between two planar surfaces](image)

**Figure 3.3:** Scheme of (left) two isolated charged surfaces of surface charge density $\sigma_0$ separated a distance $D$ in the water. The counterion density $\rho_z$ and electrostatic potential $\psi_z$ profiles (right). The overlap between the counterions of the two surfaces leads to increase of the osmotic pressure. The osmotic pressure at the midplane ($z = 0$) corresponds to $P(D = \infty) = 0$. $\rho_0$, $\psi_0$ are ion density and potential at the surface respectively.
The interaction pressure $P$ between two equally charged surfaces of the surface charge, $\sigma_0$, in an electrolyte solution as it is shown in Fig.3.3. At any position $z$, the interaction pressure $P$ is related to $\mu$ via the well-known thermodynamic relation $(\partial P/\partial \rho)_{z,T} = \rho(\partial \mu/\partial \rho)_{z,T}$ where $\mu$ is given by Eq.3.5. The change in the pressure at $z$ on bringing two plates from infinity ($P(z = \infty) = 0$) to a separation $D$ including $D = \infty$ at constant temperature $T$ is, therefore: 

$$P_z(D) - P_z(\infty) = -\frac{1}{2} \varepsilon \varepsilon_0 \left( \frac{d\psi}{dz} \right)^2_{z(D)} + k_B T \rho_z(D) + \frac{1}{2} \varepsilon \varepsilon_0 \left( \frac{d\psi}{dz} \right)^2_{z(\infty)} - k_B T \rho_z(\infty)$$

(3.22)

This equation gives us the pressure $P$ at any point $z$ between two surfaces at a distance $D$.

$$P_z(D) - P_z(\infty) = -\frac{1}{2} \varepsilon \varepsilon_0 \left[ \left( \frac{d\psi}{dz} \right)^2_{z(D)} - \left( \frac{d\psi}{dz} \right)^2_{z(\infty)} \right] + k_B T [\rho_z(D) - \rho_z(\infty)]$$

Here, the first square bracket represents the electrostatic field energy contribution and it is always negative (attractive). The second square bracket is the entropic (osmotic) contribution to the force and it is always positive (repulsive). By using ion density (Eq.3.11):

$$\sum_i \rho_{zi} - \rho_{mi} = \frac{\varepsilon \varepsilon_0}{2k_B T} \left( \frac{d\psi}{dz} \right)^2$$

we get

$$P_z(D) = k_B T \left[ \sum_i \rho_{mi}(D) - \sum_i \rho_{mi}(\infty) \right] = k_B T \left[ \sum_i \rho_{mi}(D) - \rho_{i,\infty} \right]$$

(3.23)

where $P$ is the excess osmotic pressure of the ions in the mid-plane over the bulk pressure. $\rho_{i,\infty}$ is the bulk electrolyte concentration. To find the total concentration of ions at the mid-plane $\rho_{mi}(D)$, the analytic assumption of Verwey, and Overbeek [Verwey and Nes, 1948] is used.

$$P = k_B T \rho_{i,\infty} \left[ e^{\frac{Z_i e \psi_m(D)}{k_B T}} - 1 \right]$$
where $\psi_m(m)$ is the electrostatic potential in the middle of both surfaces ($z = 0$). For a $n:n$ salt such as NaCl, Eq. 3.23 can be simplified to

$$P_{PB}(D) = k_B T \rho_\infty \left[ e^{-\frac{ne \psi_m(D)}{k_B T}} + e^{-\frac{ne \psi_m(D)}{k_B T}} - 2 \right] = k_B T \rho_\infty \left( 2 \sinh \left( \frac{ne \psi_m(D)}{2k_B T} \right) \right)^2$$

(3.24)

For $(ne \psi_0 \ll k_B T)$ i.e. small surface charge potentials or large surface separation $(D \gg \kappa^{-1})$

$$P_{PB}(D) \approx k_B T \rho_\infty \left( \frac{ne \psi_m(D)}{2k_B T} \right)^2$$

(3.25)

The electrostatic potential at mid-plane $\psi_m(D)$ can be approximated using Eq. 3.15

$$\psi_m(D) = 2 \frac{\psi_m(D/2)}{2} = 2 \frac{4k_B T}{ne} \tanh \left( \frac{ne \psi_0}{4k_B T} \right) e^{-\frac{\kappa D}{2}}$$

(3.26)

By inserting Eq. 3.26 into Eq. 3.25, the repulsive pressure between two planar surfaces is

$$P \approx k_B T \rho_\infty \left( 8 \tanh \left( \frac{ne \psi_0(D)}{4k_B T} \right) e^{-\frac{\kappa D}{2}} \right)^2 = 64 \frac{k_B T}{ne} \tanh^2 \left( \frac{ne \psi_0(D)}{4k_B T} \right) e^{-\kappa D}$$

(3.27)

Using the Derjaguin approximation again Eq. 3.2, in terms of force between two charged planar surfaces, the interaction energy per unit area

$$W_{DH}(D) = \frac{F_{DH}(D)}{2\pi R} = \frac{N_A k_B T c}{\kappa} \tanh^2 \left( \frac{ne \psi_0(D)}{4k_B T} \right) e^{-\kappa D} = \frac{F_0}{2\pi R} e^{-\kappa D}$$

(3.28)

where $N_A$ is the Avogadro constant and $c$ is the salt concentration in Mol.

$$\frac{F_{DH}(D)}{2\pi R} = 0.0482 \sqrt{I_{NaCl} \tanh^2 \left( \frac{\psi(mV)}{103} \right) e^{-\kappa D}}$$

(3.29)
charge density is always above the expected value. Thus the constant charge (CC) boundary condition takes into account that charge density of the surface $\sigma_0$ is constant and the Grahame equation could be solved to obtain the distance relation between $\psi_0$ and $\sigma_0$. The Debye-Hückel could be written in this case as

$$
\psi_0 = \frac{2k_BT}{Ze} \cdot \frac{\sigma_0}{\sqrt{8k_BT\epsilon\varepsilon_0\rho_\infty}} \tanh^{-1} \left( \frac{\kappa D}{2} \right)
$$

(3.30)

which can be applied to calculate Eq.3.28. Both (CP) and (CC) boundary conditions are identical when the surface separation $D$ is much larger than Debye length.

For two surfaces with different surface potentials $\psi_{0,1}$, $\psi_{0,2}$, Eq.3.27 and Eq.3.28 works well if both surfaces have the same surface charge sign and both surface potentials are much smaller than the thermal energy. Therefore both equations could be rewritten again for two surfaces as [Israelachvili, 1991]:

$$
P_{DH}(D) = 64k_BT\rho_\infty \tanh \left( \frac{ne\psi_{0,1}(D)}{4k_BT} \right) \tanh \left( \frac{ne\psi_{0,2}(D)}{4k_BT} \right) e^{-\kappa D}
$$

(3.31)

$$
W_{DH}(D) = \frac{F_{DH}(D)}{2\pi R} = 64\frac{N AK_BTc}{\kappa} \cdot \tanh \left( \frac{ne\psi_{0,1}(D)}{4k_BT} \right) \cdot \tanh \left( \frac{ne\psi_{0,2}(D)}{4k_BT} \right) e^{-\kappa D}
$$

(3.32)

At low surface potential, $\psi_0 < 25$ mV, for two planar surfaces, all of the above equations are simplified to

$$
P \approx 2\epsilon\varepsilon_0 K^2 \psi_0^2 e^{-\kappa D} = \frac{2\sigma^2}{\varepsilon\varepsilon_0} e^{-\kappa D}
$$

$$
W \approx 2\epsilon\varepsilon_0 K^2 \psi_0^2 e^{-\kappa D} = \frac{2\sigma^2}{\kappa\epsilon\varepsilon_0} e^{-\kappa D}
$$

These equations are valid for all salt types like 1:1, 2:2, 3:1, or even mixtures, and $\sigma_0$ and $\psi_0$ are related by $\sigma_0 = \varepsilon\varepsilon_0 K^2 \psi_0$.

The cause of the repulsive interaction between two identically charged surfaces in a solvent with ions is not electrostatic but entropic (osmotic). If an isolated surface which is initially uncharged is immersed in the aqueous solution, the surface groups dissociate. These counter-ions disassociate from the surface, but the attractive Coulomb forces attract them. The repulsive osmotic pressure between the counter-ions keeps the diffuse double-layer. This osmotic pressure forces the counter-ions to leave the surface and stay away from each other in order to raise their configuration entropy. To bring two such surfaces together, the counter-ions are forced to back
onto the surface in contradiction to their desired equilibrium state (osmotic repulsion), but osmotic repulsion is preferred by the electrostatic interaction. A similar action can be established for polyelectrolyte brushes when two surfaces covered with polymer approach each other. When the outward segments start to overlap, this interaction frequently leads to a repulsive osmotic force due to the undesirable entropy correlating with compressing the chains between the surfaces [Israelachvili, 1991].

### 3.3 Conformation of adsorbed polymers

The adsorption of polymer onto an interface is associated with a chain confinement and an increase in the free energy and entropy loss (as $F = U - TS$). To get a stable chain conformation, this free energy should be minimized by attractive interaction to the surface at constant temperature $T$ and inner energy $U$. The monomer-surface-bond is favored over the monomer-solvent-bonds to reduce the free energy. Statistically, the adsorbed polymer is described in the terms of simple configurations (loops, trains, and tails (cf. Fig. 3.4, left) [Fleer et al., 1993; Bohmer et al., 1990]. The fractions of trains, loops, and tails depend on the polymer and surface properties. An adsorption of short rigid polymer ($L_p \approx L_C$) gives a conformation of a few loops and tails. For softer polymer ($L_p \ll L_C$) the loop and tail fractions are increased. At strong monomer-surface interaction as polyelectrolytes at low electrostatic screening, a compacted polymer layer is formed. For weak monomer-surface interaction, the thickness of the adsorbed polymer layer is increased. The grafted polymers contain a hydrophobic anchor and a (hydrophilic) polyelectrolyte. Different chain conformations of grafted polymers are possible depending on the distance $s$ between the grafting points of the polymer and the monomer interface affinity (cf. Fig. 3.4, right). The adsorbed polymer chains show pancake conformation at strong monomer-interface affinity. At low affinity and $s > 2R_g$, no confinement occurs and the chain shows mushroom conformation. At $s < 2R_g$, the chains feel a confinement which leads to a steric repulsion between them so they form a polymer brush. The polymer brush could be a much-stretched layer. The steric repulsion of the neutral polymer brushes is in nature and the brush thickness $L$ is on the order of $R_g$. On the other hand, the thickness $L$ of polyelectrolyte brushes can be as much as one half of the contour length $L_C$ due to the strong osmotic pressure.
3.4 Steric Forces of adsorbed polymers

Figure 3.4: Theoretically, the adsorbed polymer is described in the terms of simple configurations: loops, trains, and tails (left) [Bohmer et al., 1990]. Different chain conformations of adsorbed polymer grafted at one or more points to the surface. For a strong monomer-surface affinity, a pancake conformation is formed. At low monomer-surface affinity a mushroom \((s > 2R_g)\) or polymer brush \((s < 2R_g)\) conformation is exhibited (right) [Block, 2010].

To describe the electrostatic and steric forces which act between two surfaces covered with neutral polymers, two different approaches are introduced. The action of the monomers is described using the effective potential and the monomer density \(\rho_m(r)\) is calculated by minimizing the total system free energy \(F\); this is defined as the mean field approach [Flory, 1969; Netz and Andelman, 2003]. The second approach is scaling theories which divide a polymer into a sequence of blobs [De Gennes, 1979]. So for both approaches, and if the adsorption energy is small compared to \(k_B T\) due to a weak monomer-surface interaction, the diffusion of the polymer layer decays by increasing the distance \(z\) to the planar surface. This defines the volume fraction \(\phi(z)\) as [de Gennes, 1980]:

\[
\phi(z)_{\text{scaling}} \propto z^{-4/3} \quad (3.33)
\]

\[
\phi(z)_{\text{mean field}} \propto z^{-z/D_{\text{Lay}}}
\]

where \(D_{\text{Lay}}\) represents the thickness of the adsorbed polymer.

3.4 Steric Forces of adsorbed polymers

If two surfaces approach each other, their protrusions become increasingly limited to a smaller region of space and, without existence of other interaction, a repulsive force arises causing undesirable entropy. The cause of these forces is essentially entropic or osmotic, and are called “thermal fluctuation,” “entropically driven,”
or “protrusion” forces. An additional form of a thermal diffuse interface happens when polymer chains grafted to a surface, dangle out and thermally mobile into the solution. By approaching two surfaces, the entropy of these restricting chains leads to a repulsive entropic force. The overlapping of the dangling polymer chains is the “steric” or “overlap” repulsion. Even these fluctuations are in the range of a few angstroms, which is enough to affect the molecular structure of the surfaces and the forces between them. Depending on the shape and interaction of the molecule at an interface, different kinds of fluctuations and resultant protrusions can be raised. Some of these protrusions can have rather large amplitudes [Israelachvili, 2011].

For neutral polymer brushes attached to a planar surface, a scaling approach is used to show that the fundamental length scale of the blobs is given by the distance $s$ between the grafting points [Alexander, 1977]. The grafted polymers have a mushroom conformation in the interval $a > z > s$ where $a$ is the monomer size and the volume fraction profile $\varphi(z)$ is given by [de Gennes, 1980]

$$\varphi(z) \propto \frac{1}{s^2} z^{2/3} \text{ for } a > z > s.$$ 

The blobs distribution of the brush is homogeneous after traveling the distance away from the surface and the volume fraction profile $\varphi(z)$ is constant in this region

$$\varphi(z) \propto s^{-4/3} \text{ for } s < z < L$$

The volume fraction profile of a neutral polymer brush is approximated by a step profile and the scaling theory of Alexander and de Gennes or AdG theory is written as

$$\Phi_{step}(z) \propto \begin{cases} 
N/(L \cdot s^2) & 0 < z < L \\
0 & \text{elsewhere}
\end{cases}$$

The step profile leads to the scaling law for the thickness $L$ of a neutral polymer brush:

$$L_{AdG} \propto N \cdot (s^2)^{-1/3}$$

The interaction between two planar surfaces covered by an identical neutral polymer brush (symmetric case) is calculated as [de Gennes, 1987]

$$P_{AdG, symm}(D) = \frac{k_B T}{s^3} \left[ \left( \frac{D}{2L} \right)^{-\frac{3}{2}} - \left( \frac{D}{2L} \right)^{\frac{3}{2}} \right] \text{ for } D < 2L$$
3.4 Steric Forces of adsorbed polymers

\[ W_{AdG,\text{symm}}(D) = \frac{F_{AdG,\text{symm}}(D)}{2\pi R} = \frac{8k_BT L}{35s^3} \left[ 7 \cdot \left( \frac{D}{2L} \right)^{-\frac{7}{4}} + 5 \cdot \left( \frac{D}{2L} \right)^{\frac{7}{4}} - 12 \right] \]

And in the range between \(0.2 \leq D/2L \leq 0.9\) the osmotic pressure and the energy are reduced to exponential decay:

\[ W(D) = \frac{F(D)}{2\pi R} \approx \frac{100k_BT L}{s^3} e^{-\left(\pi/L\right)D} \]

This theory also describes the interaction of a neutral polymer brush with dissimilar surfaces [O’Shea et al., 1993]. The interaction between two planar surfaces in the asymmetric is given by [Butt et al., 2006]

\[ P_{AdG,\text{asymm}}(D) = \frac{k_BT}{2s^3} \left[ \left( \frac{D}{L} \right)^{-\frac{7}{4}} - \left( \frac{D}{L} \right)^{\frac{7}{4}} \right] \quad \text{for } D < L \]

\[ W_{AdG,\text{asymm}}(D) = \frac{F_{AdG,\text{asymm}}(D)}{2\pi R} = \frac{2k_BT L}{35s^3} \left[ 7 \cdot \left( \frac{D}{L} \right)^{-\frac{7}{4}} + 5 \cdot \left( \frac{D}{L} \right)^{\frac{7}{4}} - 12 \right] \]

The force profile is a non-linear function and it is approximated at intermediate surface separations \((0.2 \leq D/L \leq 0.9)\) by an exponential function with a decay length given by \(\lambda^{-1} = -L/\pi\) (symmetric) and \(\lambda^{-1} = -L/2\pi\) (asymmetric) where \(L\) is the brush thickness [Israelachvili, 1991].
4 Measurement Fundamentals and Setups

4.1 Atomic Force Microscopy (AFM)

AFM is a developed form of the scanning tunneling microscopy (STM). A requirement of STM is electricity between the tip and sample. Many materials of interest are non-conducting. Therefore, instead of measuring a tunneling current between the tip and the sample, one can measure the interaction force between the front atom of the tip and the substrate atoms by gently scanning across the surface [Binnig et al., 1986]. AFM measures the interaction between the cantilever tip and the surface in order to determine different surface properties (topography, elasticity, surface forces, surface charge density, surface potential, etc.). There are two basic types of interactions between the tip and the substrate when the tip approaches the sample (cf. Fig. 4.1). First, the lead atom on the tip interacts with the lead atom on the substrate causing an atom-atom or atomic force interaction. Second, are the collective tip-substrate interactions. These forces can be attractive or repulsive interaction forces, depending on the properties of the tip and substrate. At the contact point between the tip and the substrate, and because of the repulsive or attractive interaction forces, the cantilever will be deflected.

4.1.1 Fundamental setups

AFM consists of a 3-D piezo scanner, a probe with a mounted cantilever, a position sensitive detector, a laser beam, and an AFM controller (cf. Fig. 4.2). The piezo scanner can be extended to 3-D by applying an external voltage (piezoelectric effect) to move the sample. The cantilever holder (probe) is fixed in the top of the moving sample (Veeco Multimode). To detect the cantilever deflection due to the tip-substrate interaction, a position sensitive detector is used. It is based on a four-quadrant photodiode and light lever method to detect laser intensity and convert it to voltage [Meyer and Amer, 1988].
The reflected laser beam on the photodetector is shifted by the cantilever deflection. As a result, an intensity shift in each quadrant of the photodiode is recorded, while the sum of the intensity over the 4 quadrants stays maximum and constant. The vertical and horizontal voltage shifts are proportional to the vertical and horizontal deflection of the cantilever. The measured force depends, among other parameters, on the geometry and the elasticity of the cantilever. Commercial cantilevers are made of silicon or silicon nitride in a precise etching process, wherein the tip thickness can vary between 2 nm and 100 nm depending on the application purpose. The elasticity of the cantilever is measured by the spring constant, which is in the range of 0.01 Nm$^{-1}$ to 100 Nm$^{-1}$. Depending on the nature of the sample and experimental requirements, AFM can be used in different operating modes. Basically, there are two operation modes, imaging mode: and spectroscopic mode.
4.1.2 Elastic properties and calibration of the AFM cantilever

The knowledge of the spring constant $k$ of the cantilever is a necessary requirement for the analysis of force-distance curves. In this work, rectangular cantilevers were used. According to Stokey, the spring constant $k$ of a homogeneous bar of length $l$ with a rectangular shape is modeled as [Stokey, 1989]

$$k = \frac{Eh^3b}{4l^3} \quad (4.1)$$

where $b$ and $h$ are the width and thickness of the cantilever respectively, and $E$ is Young’s modulus. Since the spring constant of the cantilever provided by the manufacturer has a high uncertainty and the attached $\text{SiO}_2$ sphere on the front of the tipless cantilever influences strongly the spring constant, $k$ of each cantilever has to be measured separately. For an accurate calculation of the spring constant, the dimensions and the bending properties of the cantilever have to be included.

The differential equation of a rod vibrating with a small amplitude is given by

$$EI \frac{\partial^4 z(x, t)}{\partial x^4} + \mu \frac{\partial^2 z(x, t)}{\partial t^2} = F(x, t) \quad (4.2)$$

$F$ is the externally applied force per unit length, $z(x, t)$ is the deflection of the cantilever (cf. Fig. 4.2), $t$ is the time, $\mu$ is the mass per unit length of the bar and $I$...
4.1 Atomic Force Microscopy (AFM)

is the moment of inertia. If the external force is zero and the cantilever is in vacuum
the solution of the equation is [Butt and Jaschke, 1995]

\[
z(x, t) = \sum_i C_i \cdot \sin(\omega_{i,vac}t + \varphi_i) \cdot \Phi_i(x) = \sum_i q_i(t) \cdot \Phi_i(x)
\]

(4.3)

\(z(x, t)\) is the deflection of the cantilever described by two harmonic oscillators func-
tions \(q_i(t)\) and \(\Phi_i(x)\). The resonant frequencies of the cantilever for \(i\)-th mode \(\omega_{i,vac}\)
is

\[
\alpha_i^4 = \frac{\mu \omega_{i,vac}^2 l^4}{EI}
\]

(4.4)

where \(I\) is the moment of inertia and it is \(I = \frac{h^3b}{12}\) for a rectangular bar. If the
bar has one free end, \(\alpha_i\) fulfills \(cos\alpha_i \cdot cosh\alpha_i = -1\). By neglecting the damping, the
resonant frequencies in vacuum \(\omega_{i,vac}\) can be calculated using Eq. 4.4 as

\[
\omega_{i,vac} = \frac{\alpha_i^2}{\alpha_i^2} \omega_{1,vac}
\]

(4.5)

Three different methods were used to calculate the spring constant \(k\) using the
averaged noise spectrum:

1. Cleveland modified Eq. 4.1. He excluded the cantilever thickness \(h\) which is often
unknown and used \(i = 1\). The spring constant for a rectangular cantilever for the
first mode vibration can be rewritten as follows [Cleveland et al., 1993]:

\[
k = \frac{b(l\omega_{1,vac})^3}{4} \sqrt{\frac{\rho^3}{E}}
\]

(4.6)

Here, \(\rho\) is the homogeneous density of the cantilever and \(\omega_{1,vac}\) the resonance fre-
quency of the first mode vibration at the friction-free case. The Young’s modulus
\(E\) and \(\rho\) are tabulated for most of the materials. The benefit of this method is
that both \(l\) and \(b\) can be measured using an optical microscope. This method of
Cleveland depends only on the resonant frequency of the fundamental mode. In
this work, Eq. 4.5 converts the measured frequency \(\omega_{i,fl}\) to the corresponding value
in vacuum \(\omega_{i,vac}\) then Eq. 4.6 is used to calculate the spring constant of the used
cantilever.

However, because of the surrounding flow around the cantilever, the resonance
frequency \(\omega_{res}\) is shifted, the vibration amplitude will be decreased and the peaks
of the mode spectrum will be wider. To reduce these effects, Sader introduced
a model which takes into account the hydrodynamic force which is as a result of
the surrounding medium movement. For this, a definition of Reynolds number is introduced [Sader, 1998]

\[ Re = \frac{\rho_{fl} \omega b^2}{4\eta_{fl}} \]  

(4.7)

Here, \( \omega = 2 \cdot \pi \cdot f \) where \( f \) is the frequency and \( \rho_{fl} \), and \( \eta_{fl} \) are the density and viscosity of the fluid, respectively. For small dissipation effect, the amplitude of the deflection of a cantilever of \( i \)-th mode is described as

\[ z_i(\omega) \propto \omega^2_{i,fl} \cdot \left[ \left( \omega^2 - \omega^2_{i,fl} \right)^2 + \frac{\omega^2_{i,fl}^2}{Q_i^2} \right] \]  

(4.8)

The shift of the resonance frequency in the fluid surrounding medium of the fluid density \( \rho_{fl} \) is taken into account in Sader’s model [Sader, 1998]:

\[ \omega_{i,fl} = \omega_{i,vac} \left( 1 + \frac{\pi \rho_{fl} b^2}{4 \mu} \Gamma_r(\omega_{i,fl}) \right)^{-1/2} \]  

(4.9)

\( \Gamma_r(\omega) \) and \( \Gamma_i(\omega) \) are the imaginary and real part of the hydrodynamic function of the surrounding fluid \( \Gamma(\omega) = \Gamma_r(\omega) + i\Gamma_i(\omega) \) and \( \mu = \rho bh \) is the mass per unit length of the cantilever.

The quality factor of \( Q_i \) the \( i \)-th vibration mode in this model is

\[ Q_i = \left( \frac{4\mu}{\pi \rho_{fl} b^2} + \Gamma_r(\omega_{i,fl}) \right) / \Gamma_i(\omega_{i,fl}) \]  

(4.10)

In the method introduced by Sader, the spring constant is calculated by [Sader et al., 1999]

\[ k = 0.1906 \rho_{fl} b^2 l Q_i \Gamma_i(\omega_{i,fl}) \omega_{i,fl}^2. \]  

(4.11)

This model allows for a precise calculation of the spring constant. Thus, first the noise spectrum and the resonance frequencies in this work could be easily recorded in the air and converted to those in an aqueous medium. Both \( \omega_{i,fl} \) and \( Q_i \) are calculated by fitting Eq. 4.8 to the neighborhood of the \( i \)-th peak. Next Eq. 4.9 and Eq. 4.10 are applied. Finally, Eq. 4.11 is employed to get the spring constant of the used cantilever.

3. The light lever method [Butt and Jaschke, 1995] states from Paraeval’s theorem that the integration of the power spectral density is identical to the square of the
4.1 Atomic Force Microscopy (AFM)

rms of the deflection signal. The potential energy of the i-th mode using Eq. 4.3 is given as

$$W_i = \frac{k}{2} q_i^2(t) \alpha_i^4 \left( \frac{\sin \alpha_i + \sinh \alpha_i}{3} \right)^2$$

According to the equipartition theorem [Hutter and Bechhoefer, 1993], in the thermal equilibrium, the average value of $W_i$ is equal to $\frac{1}{2} k_B T$. So the average rms of the cantilever deflection can be written as:

$$\frac{1}{2} k_B T = \frac{1}{2} k < z^2 >$$

$$\downarrow$$

$$< z^2 >= \frac{12 k_B T}{k} \sum_i \frac{1}{\alpha_i^4} = \frac{k_B T}{k} \sum_i \frac{1}{\alpha_i^4} (4.12)$$

According to Butt and Jaschke, for a cantilever with one free end, $\alpha_1 = 1.88$ for the first mode of oscillation [Butt and Jaschke, 1995]. Thus Eq. 4.12 shows that 96% of the vibrational energy is stored in the first oscillation mode. In the second mode, 2.5% ($\alpha_2 = 4.69$) and in the third 0.3% ($\alpha_3 = 7.85$) of the total vibrational energy is stored [Sader, 1998]. If only the first oscillation mode is taken into account during the noise spectrum analysis, this will lead to a systematic error of 4%. To keep the systematic error smaller than 1%, the first four modes were recorded in this work (see Fig. 5.3(left)).

The light lever method measures the inclination of the cantilever (i.e., $z^*(x,t) = dz/dx$). Butt and Jaschke introduced a correction factor to calculate the rms-cantilever deflection of the i-th mode using the measured rms-inclination [Butt and Jaschke, 1995; Cook et al., 2006]

$$\chi_i^2 = \frac{< z_i^2 >}{< z_i^{*2} >} = \left[ \frac{3}{2 \alpha_i} \frac{\sin \alpha_i + \sinh \alpha_i}{\sin \alpha_i \sinh \alpha_i} \right]^2$$

$$k = \frac{0.96 k_B T}{< z_i^2 >} = \frac{0.82 k_B T}{< z_i^{*2} >} (4.13)$$

In this method, we get the area $A_i$ of the i-th mode in the power spectral density by integrating the square root of Lorentzian profile Eq. 4.8 with respect to $\omega$. Con-
Chapter 4 Measurement Fundamentals and Setups

sequently \( < z^2 > \) is calculated by the sum of \( \chi_i^2 A_i \) [Block, 2010] and the spring constant of the used cantilever is calculated by applying Eq. 4.13.

### 4.1.3 Imaging Modes

**Contact mode**

In contact mode, the tip and sample surface are in contact. Gently the tip scans along the surface; the sample topography induces a vertical deflection of the cantilever (tip-sample hardcore repulsion interaction). A feedback loop keeps this deflection at a preset load force and the feedback response is used to produce a topographic image. The cantilever deflection \( z_{Defl} \) is proportional to the interaction force between the tip and the cantilever. By measuring the cantilever deflection, it is possible to evaluate the tip-surface interaction force in accordance with Hooke’s Law. In this mode, there are two possibilities: the first is the “constant height” mode that scans at a fixed small height above the surface. The constant height mode does not refer to the height of the sample, but the height of the piezo scanner \( z_{Ptz} \). In this mode, the piezo scanner is unmoved in the z-direction but the cantilever deflects. This deflection changes depending on the sample structure. In this mode, the interpretation of the image is difficult because the force between the tip and the sample changes which leads to different image resolution.

The second is the “constant force” mode, which records the z-direction movement \( z_{Ptz} \) of the scanner under fixed deflection of the cantilever \( z_{Defl} \). The constant force mode is the most common mode. Using a feedback circuit keeps the deflection of the cantilever constant. The deflection is proportional to the force between the tip and the sample and is measured by the photodiode voltage. In this mode, the interaction force is constant, but the piezo displacement in z-direction changes. The interpretation of the image in this mode is easier because all the points on the image have the same force acting between the tip and the sample. The spring constant should be carefully chosen for this mode. If the applied force to the sample is high, this may lead to structural damages on the sample, especially on soft surfaces, and result in deformed images. In this mode, a soft tip material with a high resonant frequency (such as silicon nitride) is needed so that the cantilever is bent by very small forces.
4.1 Atomic Force Microscopy (AFM)

**Tapping and non-contact Mode**

Unlike contact mode, the probe tip and sample surface are not in constant contact in non-contact mode and in tapping mode. Rather, these two methods belong to the family of dynamic imaging modes, wherein the cantilever usually acts as a damped harmonic oscillator. As it is shown before (Sec. 4.1.2), the cantilever can be induced to oscillate with several resonant frequencies $\omega_{i,fl}$ of the $i$-th vibration mode with a quality factor $Q_i$. These resonant frequencies depend on the cantilever properties and the surrounding media as it was introduced before by Eq. 4.8. If $F_0$ is the exciting force with the excitation frequency $\omega$, and the damped oscillator movement can be described by the differential equation as

$$\frac{d^2}{dt^2} z(l, t) + \beta_i \frac{d}{dt} z(l, t) + \omega_{i,fl}^2 \cdot z(l, t) = \frac{1}{m_i^*} (F_0 \cos(\omega \cdot t) + F(D + z(l, t)))$$  \hspace{1cm} (4.14)

$F(D+z)$ is the interaction force between the surface sample and the tip as a function in the surface separation $(D+z)$ which causes a cantilever deflection $z$, $\beta_i$ is the damping coefficient ($\beta_i = \omega_{i,fl}/Q_i$) in Sader’s model, and $m_i^*$ stands for the effective mass of the cantilever. For the harmonic oscillator without any losses ($Q_i \rightarrow \infty$), the resonance frequency is given by $\omega_{i,vac}^2 = \frac{k}{m_i}$ [Block, 2010]. By applying Eq. 4.1, Eq. 4.4 the effective mass is given as

$$m_i^* = \frac{3}{\alpha_i} m$$

This gives for the fundamental mode $(i=1, \alpha=1.88)$ an effective mass of 0.24 $m$ in vacuum [Butt and Jaschke, 1995]. In the stationary case $F(D - z = 0)$, Eq. 4.14 can be solved with the following approach

$$z(l, t) = Z_i(\omega) \cos(\omega \cdot t + \varphi_i)$$

This defines a harmonic oscillation with an amplitude of [Demtröder, 2006]:

$$Z_i(\omega) = \frac{F_0}{m_i^*} \left[ (\omega^2 - \omega_{i,fl}^2)^2 + \omega^2 \beta_i^2 \right]^{-1/2}$$

and the phase

$$\tan \varphi_i(\omega) = -\frac{\beta_i \omega}{\omega_{i,fl}^2 - \omega^2}$$
Experimentally, $\omega_{i,res}$ of the tapping mode is often chosen for the resonant frequency of a fundamental mode of oscillation. This is positioned at the maximum value of the amplitude which is defined as:

$$\omega_{i,res}^2 = \omega_{i,fl}^2 - \beta_i^2 / 2$$

For small amplitudes, Eq. 4.14 can be simplified to

$$\frac{d^2}{dt^2} z(l,t) + \beta_i \frac{d}{dt} z(l,t) + \omega_{i,force}^2 z(l,t) = \frac{F_0}{m_i} (\cos(\omega.t))$$

And if this is applied, it will give

$$\omega_{i,force}^2 = \omega_{i,fl}^2 - \frac{F(D)}{m_i}$$

The frequency spectrum of the cantilever is introduced in this case by [Albrecht et al., 1991]

$$\omega_{i,res}^2 = \omega_{i,fl}^2 - \frac{F'(D)}{m_i} - \frac{\beta_i^2}{2} \quad (4.15)$$

Depending on the properties of the interaction between the sample surface and the tip, the resonance frequency $\omega_{i,res}$ is shifted to higher values (repulsive interactions, $F'(z) < 0$) or lower values (attractive interactions, $F'(z) > 0$) according to Eq. 4.15 [Albrecht et al., 1991].

For non-contact imaging, in the case of attractive interaction between the tip and sample, the drive frequency $\omega$ is chosen to be a little higher than the resonance frequency $\omega_{i,res}$. In the opposite case of repulsive interaction, the cantilever is driven with a frequency $\omega$ slightly lower than the resonance frequency.

The resonance frequency of the cantilever $\omega_{i,res}$ is shifted due to the interaction in the direction of the constant drive frequency $\omega$ and the oscillation amplitude of the tip is reduced without touching the surface. So if the oscillation amplitude of the tip is extremely high, the tip-surface separation is reduced and the separation will be increased for the small oscillation amplitude. Similar to contact mode, recording the voltage map changes allows for surface topography imaging. The tip in non-contact mode never touches the sample surface; but in the intermittent contact or tapping mode, and if the force is very small, the tip may momentary touch the sample. The vibration amplitude is reduced again due to the hard core repulsion. The tip shortly taps the surface on every oscillation and the reduction
of the vibration amplitude is detected and used as feedback for the proportional–
integral–derivative (PID) regulator. The typical range of the spring constant in this
mode is 10-50 Nm\(^{-1}\) with excitation frequencies of 100-400 kHz and an amplitude
of 10-150 nm. A significant advantage of the dynamic modes over the contact mode
is the reduction of lateral shear forces on the sample surface, allowing, for example,
the most nondestructive imaging of biological surfaces.

4.2 Diffusion

Consider a number of particles in the unmixed state which diffuse randomly in a
volume. Thus, due to the Brownian motion, the particle current density or the
diffusion flux \(J\) is proportional to the concentration gradient:

\[
J = -D \cdot \nabla c, \text{ and in 1 D one obtains } J = -D \frac{\partial c}{\partial x}\]

(4.16)

This is well-known as Fick’s law of diffusion where \(D\) is the diffusion constant and
\(c\) is the particle concentration. \(c(x, t)\) depends on time. The continuity equation is
given by

\[
\frac{\partial c}{\partial t} + \nabla J = 0
\]

We can use this relationship with Eq. 4.16 to describe the diffusion processes with
time-dependent concentration gradients, Fick’s 2\textsuperscript{nd} law of diffusion processes and
results from the insertion of Fick’s 1\textsuperscript{st} law.

\[
\frac{\partial c}{\partial t} = D \nabla^2 c
\]

(4.17)

and in one dimension along the x-axis

\[
\frac{\partial c}{\partial t} = -\frac{\partial J(x)}{\partial x} = D \frac{\partial^2 c(x)}{\partial x^2}
\]

(4.18)

Fick’s 2\textsuperscript{nd} law of the diffusion is a second order differential equation. By infinite
integration, the solution of this equation provides a time- and location-dependent
Gaussian function which is the probability of the particle to exist at \(x(t)\).

\[
c(x, t) = \frac{M}{2\sqrt{\pi}Dt} e^{-\left(\frac{x^2}{4Dt}\right)}
\]

(4.19)
For the total number of diffused particles $M$ which is constant, the following boundary condition has to be applied:

$$M = \int_{-\infty}^{+\infty} c(x,t)dx = \text{const.}$$

Using the concentration profile Eq. 4.19, the mean square displacement of the particle as a function of time is given by

$$\langle x^2 \rangle = 2Dt$$

(4.20)

The diffusion constant $D$ of colloidal particles such as gold nanoparticles diffused in a liquid can be described by the Stokes-Einstein equation:

$$D = \frac{k_BT}{6\pi\eta r_h}$$

(4.21)

Here, $\eta$ is the dynamic viscosity of the medium and $r_h$ represents the hydrodynamic radius of the diffused particle. The diffusion and adsorption behavior of electrically charged colloidal particles of an opposite interface is investigated. Crank showed that the diffused amount of particles $M$ at time $t > 0$ which leave a planar source of particles with a concentration $c_0$ $(t = 0, x = 0)$ or the bulk concentration is given by [Crank, 1979; Andrade, 1985]:

$$M = 2c_0 \sqrt{\frac{D \cdot t}{\pi}}$$

(4.22)

The adsorption process of charged particles can also be described by Eq. 4.22. This description assumes that during the absorption process, any particles that come in contact with the surface remain bound to it [Crank, 1979; MacRitchie and Alexander, 1963]. The adsorbed amount of particles in a specific time, which is called the surface density $\Gamma(t)$:

$$\Gamma(t) = 2c_0 \sqrt{\frac{D \cdot t}{\pi}}$$

(4.23)

This describes the surface density as a function of the square root of time.
4.3 UV-Vis spectroscopy

Light interaction

Many different phenomena can happen when light interacts with matter such as absorption, reflection, scattering, transmutation or even fluorescence emission. Ultraviolet and visible light (UV-vis) (energy, 1-5 eV) excite outer electrons of an atom or delocalized $e^{-}$ in orbitals to higher energy levels; UV-vis radiation corresponds to the electron excitation. As the light is absorbed and transformed to internal energy through an absorber, the light intensity is decreased. The wavelength at which the incident photon is absorbed to excite the electrons correspond to the energy levels separation of the absorbing materials. Absorbance spectroscopy is a unique technique that uses the analytic compound [Hollas, 2004].

Beer-Lambert Law

The absorption contribution over the path length of light $d$ in the studied medium is described using the Beer-Lambert law [Drake, 2006]:

$$I(\lambda) = I_0(\lambda) \cdot e^{-\gamma(\lambda)d}$$

where $I$ is the intensity of the light transmitted through the sample and $I_0$ is the intensity of the incident light, $\gamma$ is the extinction coefficient (or absorption coefficient with neglect reflection and scattering effects of nanoparticles). This is usable

Figure 4.3: UV-vis absorption. The intensity of the incident light $I_0$ decays to $I$ due to absorption, reflection and scattering processes after passing through a sample with thickness $d$. 

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for highly monochromatic and collimated radiation in an optically homogeneous medium [Sommer, 1989]. The absorbance of the medium is proportional to the incident and transmitted intensities in a logarithm form, and this directly depends on the media properties which the light is passed through:

\[ A = \log_{10} \left( \frac{I_0}{I} \right) = \frac{1}{\ln(10)} \epsilon c_0 d \]

where \( \epsilon \) and \( c_0 \) are the molar decadic extinction coefficient and the species concentration, respectively. The molar extinction coefficient is an important molecular property in a given solvent at a specific pressure and temperature.

### 4.4 X-ray Reflectivity

Structural information like roughness and film thickness can be obtained with X-ray reflectivity (XRR) on Å level. It is well-known as a non-destructive and non-contact reflectivity technique. XRR depends on the interference between beams reflected from different interfaces. By detecting this reflection interference, in addition to crystalline film material, amorphous and liquid samples can be studied. X-rays interact with electrons of an atom and reflectivity measurements are sensitive to the inhomogeneity of the electron length density. Different to AFM, XRR delivers information averaged over a large volume. XRR is sensitive to the total film thickness, surface, roughness and average electron density (per Å³). It is also sensitive to the difference of the refractive index on the film and the substrate. It is commonly used to probe surface properties of polymers in solution, dry polymer film, organic molecules, colloidal particles and multilayer systems [Ivanova, 2010]. In the X-ray source, the cathode emitted electrons accelerate by the electric potential difference between cathode and anode. They hit the anode. Electrons are emitted from the inner shells of the atoms of the metal target (anode) and leave holes behind. Those vacancies are refilled by the outer shell electrons from dropping down from a higher energy level by emitting a photon of energy which is the X-ray photon. Most of the kinetic energy of the electrons that strike down the target is transformed into heat, less than 1% is converted into X-rays, therefore a cooling system of the anode is required. Cu Kα radiation with a wavelength of 1.54 Å corresponding to the energy of 8.8 keV is used. This X-ray energy lies far above the binding energy of most electrons of the atoms. Therefore, less energy transfer occurs; inelastic effects are negligible for X-ray radiation. Therefore, in XRR, an elastic scattering process is assumed. XRR measurements have a resolution of a fraction of nanometer, i.e., the
4.4 X–ray Reflectivity

information is gained at the molecular level.

Figure 4.4: Schematic of x-ray light interacting with a film at the interface with an incident angle \( \theta_i \), refracted angle \( \theta' \) and reflected angle \( \theta_f \) respectively (left). The electron density profile \( \rho_e(z) \) and its gradient \( \rho'_e(z) \) with the corresponding surface roughness \( \sigma \) of the film (right).

Measured reflectivity is defined by \( Q_z \) which corresponds to the vertical scattering vector or so-called wave vector transfer and is given by [Daillant and Gibaud, 2009]:

\[
|\vec{Q}_z| = |\vec{k}_f - \vec{k}_i| = \frac{2\pi}{\lambda} \left( \sin(\theta_f) + \sin(\theta_i) \right)
\]

\( k_i \) and \( k_f \) are the wave vectors of the incident and reflected light, respectively, and they define the scattering plane that is perpendicular to the surface.

In the specular case at \( \theta_f = \theta_i \), the wave vector of reflectivity is given by

\[
|\vec{Q}_z| = \frac{2\pi}{\lambda} \sin(\theta_i)
\]

The phase velocity of X-rays in a medium is higher than in a vacuum, therefore the refractive index is \( n < 1 \) (dissimilar to visible light) [Daillant and Gibaud, 2009]. To describe the interaction of X-ray wavelength \( \lambda \) with matter, the complex refractive index is introduced by

\[
n = 1 - \delta + i\beta
\]

The real part of 1–\( \delta \) of \( n \) is related to the phase–lag of the propagation wave and it
is less than the unity and $\delta(\lambda)$ describes the dispersion term and can be expressed as
\[
\delta = \left(\frac{\lambda^2}{2\pi}\right) r_e \rho_e
\]
where $\rho_e$ is the electron density of the material and $r_e = e^2/mc^2 = 2.82 \cdot 10^{-15} \text{m}^{-1}$ the classical electron radius. The imaginary part $\beta$ corresponds to the absorption or decrease of the wave amplitude. This term is positive and it is given by:
\[
\beta = \frac{\mu}{4\pi \lambda}
\]
where $\mu$ is the linear mass adsorption coefficient. For Cu Kx radiation $\delta(\lambda)$, and $\beta(\lambda)$ are on the order of $10^{-6}$ and $10^{-8}$, respectively.

Snell’s law for an incident angle $\theta_i$ (the angle between the incident beam and the surface) can be written as:
\[
\cos(\theta_i) = n \cos(\theta')
\]
where $\theta'$ is the angle between the sample surface and the refracted beam. Since $n < 1$, the X–rays incident from the air inside the film are refracted away from the normal. If X-rays are incident from the air side, and then transmitted into the substrate, they are refracted away from the surface normal. When the incident light is below a certain critical incident angle ($\theta_i \leq \theta_c$), a total external reflection happens ($\theta' = 0$) at a fraction of the degree angle of incident and incident light propagates along the surface interface. At total external reflection, the absorption is neglected ($n = 1 - \delta$), and the critical angle $\theta_c$ is written as:
\[
\theta_c = \sqrt{\frac{2\pi \rho_e r_e}{k}}
\]
Using this relation, the film electron density $\rho_e$ can be calculated where $k = \frac{2\pi}{\lambda}$, is the wave vector. The film roughness $\sigma$ is described by a normalized Gaussian distribution for the gradient of the electron density perpendicular to the surface [Tolan, 1999]:
\[
\rho_e'(z) = \frac{d\rho_e}{dz} = \frac{1}{\sigma \sqrt{2\pi}} e^{-\frac{z^2}{2\sigma^2}}
\]
where the position of the interface is at $z=0$. At $\theta_i \gg 3\theta_c$, the reflectivity $R$ is proportional to the absolute square of the Fourier transform of the density gradient:
\[
\frac{R(Q_z)}{R_F} = \left| \frac{1}{\rho_{e,\text{sub}}} \int \rho'_e e^{iQ_z z} dz \right|^2
\]

where \( \rho_{e,\text{sub}} \) is the electron density of the substrate and \( \rho'_e(z) \) is the gradient of the electron density of the film along the surface normal. The periodicity of \( Q_z \) as a function of reflectivity intensity, or so-called Kiessig fringes, relate to the film thickness \( d \) by Fig. 4.5

\[
d = \frac{2\pi}{\Delta Q_z}
\]  

\( (4.24) \)

**Figure 4.5:** Kiessig fringes as a function of the film thickness \( d \).
5 Materials, Sample Preparation and Data Analysis

5.1 Materials

The synthetic polyelectrolytes, as well as other chemicals used for this work, will be presented. The polyanion used is polystyrene sulfonate (PSS) with Na$^+$ as a counterion (Polymer Standard Service Mainz, Germany). The corresponding structural formulas are shown in Fig. 5.1. The most important properties of the polyanion PSS are listed in Tab. 5.1. The polycations used in this work are polyethyleneimine (PEI) and polydiallyldimethylammonium (PDADMA). The structural formulas of the polycations used are shown in Fig. 5.1. The branched PEI is positively charged in solution and is used exclusively as the first functionalization layer of the substrate. PEI has amino groups (NH$_3$) and a molecular weight of $M_w$(PEI) = 750 kDa (Sigma-Aldrich, Taufkirchen, Germany). The most important properties of the polycation PDADMA associated with Cl$^-$ as a co-ion are shown in Tab. 5.1.

![Figure 5.1: Structural formulas of the polyelectrolytes used in this work with the corresponding counter- or co-ions. (left) the polyanion polystyrene PSS. The polycations (middle) PEI and (right) PDADMA.](image_url)

The polyelectrolyte multilayers with different top layers were prepared by a layer-by-layer dipping method [Decher and Hong, 1991]. The persistence length $L_p$ and
the linear charge density of PSS and PDADMA differ from each other due to their different chemical structure. The persistence length \( L_p \) of PDADMA is 2.5 nm, which is about twice the persistence of PSS \( L_p = 1.2 \) nm. The monomer length is also about twice as long for PDADMA (0.54 nm) compared to PSS (0.25 nm). Both PEs are nearly 100% dissociable, resulting in a higher linear charge density for the PSS.

<table>
<thead>
<tr>
<th>M\text{w} [kDa]</th>
<th>Polydispersity</th>
<th>Polymerization degree ( N_{pol} )</th>
<th>( L_c ) [nm]</th>
<th>( R_g ) [nm]</th>
<th>D in H\text{2}O [m\text{2}/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycation PDADMA with co-ion Cl\text{−}</td>
<td>322</td>
<td>2.19</td>
<td>1994</td>
<td>1077</td>
<td>30</td>
</tr>
<tr>
<td>Polyanion PSS with counter-ion Na\text{+}</td>
<td>75.6</td>
<td>&lt; 1.2</td>
<td>367</td>
<td>91.8</td>
<td>6.1</td>
</tr>
</tbody>
</table>

Table 5.1: The properties of the polyelectrolytes used in this work. For PDADMA, the monomer length \( l = 0.54 \) nm, and persistence length \( L_p = 2.5 \) nm. For PSS, \( l = 0.25 \) nm and \( L_p = 1.2 \) nm. The radius of gyration \( R_g \) is calculated by Eq. 2.5 \( (R_g = \sqrt{\frac{L_cL_p}{3}}) \). The diffusion coefficient D is calculated in water at \( T = 300 \) K using the Stokes-Einstein equation \( D = \frac{k_B T}{6\pi\eta R_g} \) with \( \eta = 1 \) mPa s (viscosity of water).

Polished silicon wafers (100) (Si) (Cemat Silicon S.A. Warsaw, Poland) with a surface roughness of about 3 Å were used in this work. For the the Radio Corporation of America (RCA) cleaning of the silicon wafers, ammonia solution, 35% hydrogen peroxide (VWR-International, Hannover, Germany), and ultrapure water provided by an ultrapure water plant (Merck Millipore KGaA, Darmstadt, Germany, and Millipore facility (Millipore, Schwalbach, Germany) were used. In case mica was used as a substrate, its perfect cleavability parallel to the individual atomic layers could be exploited. With the help of an adhesive strip, some upper atomic layers were peeled off, forming a clean mica surface which could be immediately used without any further cleaning processes. All chemicals have the purity class per analysis and were used without further purification.

5.2 AFM: Colloidal probe and data analysis

In this work, two identical DI Multimode AFM with Nanoscope IIIa controller from Veeco (Santa Babara, CA, U.S.A.) were used. With the help of the supplied software NanoScope® IIIa, 5.31 R1 © Copyright 2006, all experimental parameters for controlling and adapting the substrate and the cantilever could be well-ordered.
Chapter 5 Materials, Sample Preparation and Data Analysis

The AFM was placed onto a granite plate (160 kg) and suspended by rubber bands for insulation against building vibrations and noise. For the thermal noise spectra measurements, the AFM was additionally stored within a closed acoustic shield with passive vibration isolation. In the DI Multimode AFM, the cantilever is held firmly inside the AFM with a special holder above the sample. To vary the cantilever position relative to the measured surface in all three spatial directions, a 3-D piezo scanner was used. For this purpose, the scanner contains several piezoelectric crystals which, operating by the piezoelectric effect, can change their thickness depending on the applied voltage. The topographical surface images recorded by the tapping are typically 512 x 512 pixels in different size and recorded in the air (laboratory conditions). Here, the maximum scanning size is 120 x 120 μm² lateral and 10 μm vertical (J scanner) or 15 x 15 μm² lateral and 3.5 μm vertical (E scanner). For the force spectroscopy, the measurements were performed on a suitable AFM fluid cell (Brucker, Billerica, MA). It was cleaned before use in Hellmanex solution (2%, T = 25°C) for 3 minutes and then rinsed off with ultrapure water. All associated components of the fluid cell, including the filling hoses, were cleaned in Hellmanex solution (2%, T = 60°C) for 30 min prior to use and then rinsed with ultrapure water. Thus, the force spectroscopic measurements could be performed inside a liquid cell with a defined environment between the cantilever and the sample surface. By using Luer fittings, silicone tubing, and a syringe, the surrounding solution was changed to measure the sample in solutions with different ionic strength.

5.2.1 Colloidal probe (CP) preparation

![Figure 5.2: (left) The colloidal probe (R = 2.5 μm) consists of a CSC12 tipless cantilever with glued SiO₂ spheres. (right) SiO₂ spheres on top of a glass slide. Images were obtained using an optical microscope.]
5.2 AFM: Colloidal probe and data analysis

For cleaning the Si wafers and microscope glass slides, the RCA standard cleaning protocol developed in 1970 was used [Kern and Puotinen, 1970]. This wet-chemical cleaning process consists of a H₂O : NH₃ : H₂O₂ solution in a ratio of 5:1:1. First, H₂O and NH₃ were heated up to about 75° C, and then H₂O₂ was added. The solution was cooled down to 60° C. The substrates were cleaned in this solution for 20 minutes and then washed off with ultrapure water. The cleaned substrates were stored in ultrapure water until the film adsorption.

For colloidal probe (CP) preparation [Glaubitz et al., 2011], an atomic force microscope (AFM, Nanowizard 3, JPK Instruments AG, Berlin, Germany) was used. The SiO₂ spheres (Bangs Laboratories, Fishers, IN) radius (R ≈ 2.5 μm), were observed by an optical microscope. A diluted solution of 0.006 wt% with 1 ml of ultrapure water was spread over a microscope glass slide which was previously cleaned according to the RCA method. After drying the adsorbed SiO₂ spheres film inside the laminar air stream of a drying box (BDK Luft- and Reinraumtechnik GmbH, Sonnenbühl-Genkingen, Germany), aggregated and isolated SiO₂ spheres were found (Fig. 5.2, right). Second, a thin tungsten wire (width <1 mm) was used to bring a thin layer of UV-curable epoxy glue (NOA68, Norland Adhesives, Cranbury, NJ) to clean glass slide. The tipless cantilever (CSC12, k = 0.005-0.06 Nm⁻¹, MicroMash, Tallinn, Estonia) was moved toward the thin film of the UV-glue for one second by using the AFM piezo element. After retracting, a thin drop (R ≤ 2.5 μm) of the UV glue should be left on the cantilever. Using the AFM piezo element again with the help of the camera, the mounted cantilever which carried a thin drop of the UV glue was carefully aligned and brought towards an isolated SiO₂ sphere. As soon as the cantilever touched the sphere the AFM motor stopped using the piezoelectric element. A force of 5 nN was applied 5 seconds. The cantilever and the sphere were kept in contact under a radiated UV lamp (UVGL-25, VWR, Darmstadt, Germany) for 1 minute. After this partial curing process, the cantilever with the attached sphere was pulled off. Finally, the full hardening process was carried out for about 15 minutes using the UV lamp. The dimensions of CPs were measured using an optical microscope (BX61, Olympus, Shinjuku, Tokio, Japan) (Fig. 5.2, left). CP cantilevers were cleaned with argon Plasma Cleaner/Sterilizer PDC-3XG (35 W, Harrick Scientific, NY) for 1 min and were used immediately for force measurements. All force measurements were performed in an AFM liquid cell with sodium chloride solution with different concentration (NaCl from Merck, Darmstadt, Germany). Microscope slides are cleaned according to the RCA standard and freshly used.
5.2.2 The mode spectrum and the cantilever spring constant measurement

Figure 5.3: A typical deflection noise power spectral for a tipless CSC12 cantilever with glued silica sphere as a function of frequency (left). The noise spectral density with four resonance frequencies. Every resonance frequency peak is fitted (right) using the Lorentzian profile (red line) and the mean value was calculated by applying different models to determine the cantilever spring constant according to Eq. 4.6, Eq. 4.11, and Eq. 4.13.

To measure the cantilever spring constant $k$, the cantilever could be thermally excited and this thermal energy is stored in each mode of the cantilever spectrum [Hutter and Bechhoefer, 1993]. By measuring the power spectral density of the deflection noise, the cantilever mode spectrum can be obtained (Sec. 4.1.2). In this work, the mode spectrum was obtained as follows: First, the sensitivity of the cantilever was determined with respect to its deflection (bending), which is Inverse Optical Lever Sensitivity (InvOLS). The sensitivity of the recorded voltage signal by the cantilever deflection is called optical lever sensitivity OLS (unit [V/m]) and the inverse value (the inverse optical lever sensitivity, InvOLS) gives a quantitative measure of how far the cantilever has to be deflected for a certain change in voltage. For this purpose, the cantilever moved toward a freshly cleaved mica surface using AFM. A one voltage–z piezo displacement profile was measured and the slope of the constant compliance or the so-called InvOLS was found. Afterwards, to avoid any interactions between the mica surface and the cantilever during the noise spectrum measurement, the distance between the mica surface and the cantilever was first sufficiently increased. Then, the deflection noise was recorded by feeding the deflection voltage (using a signal access box) into an analog-digital converter card (National Instruments, München, Germany) of a PC. There, the deflection voltage is sampled to achieve a maximum sample frequency of 500 kHz. The sampling, the conversion
5.2 AFM: Colloidal probe and data analysis

using the InvOLS and the calculation of the power spectral density of the deflection voltage were performed by a home-written script in LabView [Block, 2010] (National Instruments, München, Germany). To improve the power spectral density resolution, the average of 100 measurements was used. Fig. 5.3 (left) shows a typical noise spectral power density profile of a CSC12 cantilever (MicroMasch, Tallin, Estonia) by taking the average of 100 individual measurements. Four resonant cantilever modes can be determined at resonance frequencies. In this thesis, the three different methods which were explained in the previous section (Sec. 4.1.2) were used to calculate the spring constant (Eq. 4.6, Eq. 4.11, and Eq. 4.13). The power spectral density profile was obtained and fitted to a Lorentz profile (cf. Fig. 5.3(right)).

5.2.3 Evaluation of force-distance curves [Block, 2010]

Figure 5.4: In the force-distance measurement, the direct measurement by AFM is the cantilever deflection over the change of the z-piezo extension (left). At the starting point of the approach curve (red line) the surfaces of CP and sample are far away enough from each other and no interaction force acts between them (baseline region). There, there is no cantilever deflection. Upon approaching nearer, the tip and the sample start to interact and the two surfaces repel each other (interaction region). If the tip approaches the surface of the sample, the repulsive force between them increases. At the point of contact between the tip and the surface, an increase of the piezo extension leads to an equal deflection of the cantilever (constant compliance region). By retracting the two surfaces reversely, the deflected cantilever begins to return to the non-deflected position and the repulsion decreases (blue line). For more retraction, an adhesion force may occur and the cantilever deflects in the other direction. At the separation point, a pulling off effect can be seen before the tip is retracted to non-interaction positions (baseline region). The constant compliance slope and the calibrated spring constant are used to convert the raw data into the force-distance profile as it is shown in the right y-axis (right).
AFM directly measures the $z$-piezo extension $z_{ptz}$ between the cantilever-sample and the cantilever deflection $z_{Defl}$. The cantilever deflection $z_{Defl}$ depends on the interaction force between the two surfaces. The cantilever is mounted in a fixed position in a holder during the measurement and it can only deflect due to the interaction forces. This cantilever deflection $z_{Defl}$ is measured by the light lever method. The sample position and its separation from the cantilever are electronically controlled using the $z$-piezo crystal element. Thus in the force-distance measurement, the surface separation $D$ is included in the $z$-piezo extension $z_{ptz}$ and the interaction force is proportional to the cantilever deflection $z_{Defl}$. A converting process from the raw data of $z_{ptz}$ as a function of $z_{Defl}$ to force $F(D)$ as a function of surface separation is needed. One complete cycle of a force-distance profile consists of two curves, approach, and separation (Fig. 5.4(red), (blue)) respectively. Although both approach and retract measurements introduce different information about the interaction forces between the two surfaces, both curves consist of three main regions:

1. The baseline region indicates the region where the surface separation is so big and no interactions between the two surfaces occur. Thus, the deflection of the cantilever $z_{Defl}$ is constant and can be set to $z_{Defl} = 0$. The precise determination of the zero line is elementary for a correct evaluation of the surface forces. Both force profiles of Fig. 5.4 already show the baseline correction. In this work, a piezoelectric displacement of $z_{ptz} = 1000$ nm was used, to make sure that in the long-range force case, at least 50% of the data points are used for the baseline determination.

2. The contact regime (constant compliance) is described as a minimal distance between the two surfaces. In this area, a further increase in the $z$-piezo displacement $z_{ptz}$ does not reduce the surface separation anymore, instead the cantilever deflects. A linear increase in $z_{Defl}$ is found by increasing $z_{ptz}$. The slope of the constant compliance gives the InvOLS or the deflection sensitivity due to the linear relation between $z_{ptz}$ and $z_{Defl}$. Adhesion interaction between both surfaces can happen in the contact area and the constant compliance will not be applied in this case.

3. Both baselines ($D \rightarrow \infty$) and constant compliance ($D \rightarrow 0$) regions define an asymptotic behavior of $z_{ptz}$ with respect to the surface separation $D$ as it is shown as dashed lines in Fig. 5.4. The interaction region between both surfaces is characterized by deviation of $z_{ptz}$ from these two lines.

To evaluate the raw data using a Matlab algorithm [Block, 2010; Block and Helm, 2008], the baseline, constant compliance and interaction regions data are used. The data analysis is carried out by a loop algorithm individually for each force-distance curve. In the next step, the mean of about 200 single force profiles is calculated. The
force curves were previously recorded under the same experimental conditions. The
transition of raw data into the force-distance profile was done using the following
steps:

In the first step, the baseline is specified and subtracted from the raw data (i.e.,
\(z_{\text{Defl}} = 0\)). This baseline correction has been made for all force-distance figures in
this thesis.

Second, the cantilever deflection is directly measured by AFM as a voltage sig-
nal. The inverse optical lever sensitivity (InvOLS in [m/V]) measures how far the
cantilever deflection should be at a certain voltage change. This InvOLS value was
measured using the constant compliance slope (hard wall interaction, \(z_{ptz} = -z_{\text{Defl}}\))
for every force profile and used to convert the voltage signal to the real cantilever
deflection \(z_{\text{Defl}}\) in nm.

Third, to get the real surface separation \(D\) between the two interacting surfaces, the
z-piezo displacement \(z_{ptz}\) must also be converted. The z-piezo displacement where
the two surfaces are in contact without cantilever deflection should be determined
\((z_0)\). This \(z_0\) is calculated by the intersection between the regression lines of the
baseline and the constant compliance. After estimating \(z_0\) in the interaction region,
the surface separation is calculated using \(D = z_{ptz} - z_{\text{Defl}} - z_0\). This is only an
approximation to define the surface distance since the minimum distance between
the two surfaces cannot be measured directly by AFM. However, this uncertainty
will not be a problem for flat surfaces. For long-range forces, steric forces, for
example, the force profile exhibits at least on the point of inflection, so the minimum
surface separation can be determined [Block, 2010].

Finally, by using the spring constants of the cantilever (see Section 4.6.1) and ap-
plying Hooke’s law \((F(D) = k \cdot z_{\text{Defl}})\), the interaction force \(F(D)\) as a function of
the surface separation \(D\) can be determined (cf. Fig. 5.4, right y label).

The resolution of force spectroscopy is limited by the thermal movement of the can-
tilever. This increases the noise level of the force-distance curve, i.e., the baseline
noise level (cf. Fig. 5.5, left). To improve this restriction of the force profiles eval-
uation, an increase in the signal-to-noise ratio could be done. Since this noise level
is based on a random process, taking the average over several force-distance curves
increases the signal-to-noise ratio (cf. Fig. 5.5, right). Before the average calculation
process, all artifact-related force profiles are sorted out manually. Then, the Mat-
lab algorithm [Block, 2010] was used to calculate the standard deviation \(\sigma_{\text{Base}}\) for
each individual force-distance curve baseline followed by median calculation of all
standard deviations. Only the force-distance profiles with \(\sigma_{\text{Base}}\) below the median
were taken into account. This process will remove all force profiles with baseline as-
associated with any small artifacts from the evaluation procedures. The smallest and largest surface separation values $D_{\text{min}}$ and $D_{\text{max}}$ were determined again for every force profile. Then, the maximum of $D_{\text{min}}$ and the minimum of $D_{\text{max}}$ were introduced as a surface separation interval of all existing force profiles $[\max (D_{\text{min}}), \min (D_{\text{max}})]$. The average value of $F(D)$ is introduced in the surface separation interval.

Finally, the averaging of the $z_{\text{Defl}}(D)$ was calculated as a simple sum process inside a selected loop. If the actual of average deflection of an $i$ curve is $z_{\text{Defl},i}(D)$, then the next average $i + 1$ is given by $\bar{z}_{\text{Defl},i+1}(D) = [i \cdot \bar{z}_{\text{Defl},i}(D) + z_{\text{Defl}}(D)] / (i + 1)$ and this value is only accepted as the new average if the standard deviation of $\bar{z}_{\text{Defl},i+1}(D)$ baseline is reduced in respect to $\bar{z}_{\text{Defl},i}(D)$. In this way, all force profiles that increase the noise level are excluded from the averaging calculation.

![Figure 5.5](image)

**Figure 5.5:** Exemplary force-distance curves were measured between two identical surfaces using AFM. The forces were normalized to the radius R of the used CP. (left) One force-distance profile. (right) An average of 100 force-distance profiles is represented. The dashed lines represent the noise levels for both profiles. Because of the averaging process, the noise level is shifted downwards by about one order of magnitude.

As it has been shown in Sec. 4.1.2, the geometry of the interacting surfaces has a great influence on the interaction force calculation. If, for example, the radius of curvature of the cantilever $R$ is in the order of magnitude of the interaction force range, then exact geometry, which is difficult and not precise, has to be taken into account in the evaluation of the force profiles [Butt, 1991]. On the other hand, and in this thesis, when $R$ is much larger than that interaction force range, the Derjaguin approximation is applied ($F(D) = 2\pi R \cdot W$). For this reason, a tipless cantilever was modified with a SiO$_2$ sphere of radius $R = 2.5 \, \mu m$ (CPT, see Section 3.1) which is very large compared to the interaction force range. In this way, it is ensured that the sample surface interacts with the SiO$_2$ sphere as two planer surfaces interact [Ducker et al., 1992; Block and Helm, 2008; Berg, 2014].
6 Surface Forces of Polyelectrolyte Multilayers

6.1 Surface forces of PSS terminated polyelectrolyte multilayers

In this chapter, the forces acting between the CP, and polyelectrolyte multilayer film consisting of a different number of layer pairs N are presented. For symmetric measurements, the sample and CP are covered by the respective polyelectrolyte and the same layer pairs N. For asymmetric measurements, a CP with different coverage was used and will be mentioned separately for every measurement. The PEM films were prepared by sequential adsorption of oppositely charged polyelectrolyte. Polyelectrolytes were PEI (polycation, $M_w = 750$ kDa), PDADMA (polycation, $M_w = 322$ kDa, $L_c = 1070$ nm), and PSS (polyanion, $M_w = 75.6$ kDa, $L_c = 91.8$ nm). The polyelectrolyte multilayers were prepared from solutions with neutral pH and 0.1 M NaCl. The branched PEI was used for a first functionalization of the substrate. More information about the preparation and measurement were given in chapter 4. This chapter is organized as follows:

A comparison between the forces measured between of polyelectrolytes with one and five layers terminated with PDADMA as a function of the ionic strength will be introduced in Sec.6.1.1. The forces measured between of polyelectrolytes with four layers terminated with PSS as a function of the ionic strength will be shown also in this part. The effect of increasing the number of layer pairs on the surface conformation, surface charge density, and surface potential of the PSS terminated film will be discussed in Sec.6.1.2. The effect of increasing the number of layer pairs and the ionic strength in the solution on the PDADMA terminated film is also provided in Sec.6.2.
6.1.1 PEI / PSS / [PDADMA / PSS] terminated with PSS and PDADMA

Figure 6.1: Force-distance profiles (dots) recorded in sequence with increasing NaCl concentrations in water, as indicated by the arrows, and acting between two surfaces covered with a) PDADMA, b) PEI / PSS / [PDADMA / PSS], and c) PEI / PSS / [PDADMA / PSS] / PDADMA (physisorbed from 100 mM NaCl solution). Measurements were performed by averaging over 100-150 approach curves for each salt solution. The averaged force curves are shown here. The force profiles were fitted to the linearized solution of the double layer repulsion (lines, Eq.6.1) using the constant potential approximation. All forces are repulsive for all ion concentrations below 1 M NaCl, except for PDADMA which started to show attractive forces at 5 mM (not shown in this figure). The decay length (d) is very similar to the theoretical Debye length ((d, line), (Eq.3.21)) up to an ion concentration of 100 mM.

For all ion concentrations below 1 M NaCl, purely repulsive forces acting between two surfaces covered with PDADMA, PEI / PSS / [PDADMA / PSS], and PEI / PSS / [PDADMA / PSS] / PDADMA are observed and introduced in a logarithmic scale (cf. Fig.6.1), except for PDADMA, which starts to show attractive forces at 5
mM. By reducing the ionic strength again to 0.05 mM and water alone respectively, the repulsive forces become more long-ranged and the attractive forces disappear (cf. Fig. 6.2).

**Figure 6.2:** Force-distance profiles acting between two surfaces covered with PDADMA, (physisorbed from 100 mM NaCl solution) and recorded in sequence at 5 mM, 0.05 mM, and pure water. At 5 mM a negative force appears and by reducing the ionic strength to 0.05 mM or pure water, the force disappears again. The forces get more long-ranged by washing the NaCl away with water.

The repulsive force profiles of the three different surfaces were fitted to the linearized solution of the double layer repulsion (Eq. 6.1) using the constant potential approximation. It is found that the measured decay length (cf. Fig. 6.1(d)) is very similar to the theoretical Debye length $\kappa^{-1}$ (Eq. 3.21) up to ion concentration of 100 mM (preparation concentration) except for surfaces covered with PDADMA. The surface potential $\psi_0$ was calculated by applying Eq. 6.1 to the direct force profiles (Fig. 6.1, a to c). The surface charge densities $\sigma_0$ were calculated by Grahame’s equation Eq. 6.2 to the fitted surface potential. There is no significant change in the surface charge density and surface potential between the surfaces covered with PDADMA and PEI / PSS / [PDADMA / PSS]$_1$ / PDADMA (cf. Sec. 6.1.1). These surfaces are positively charged as is expected for PDADMA terminated surfaces. For PEI / PSS / [PDADMA / PSS]$_1$ film with PSS as a top layer, the obtained surface charge and surface potential (Fig. 6.3(top), Tab. 9.5) are higher than the values observed by [Block, 2010] for one layer PSS (physisorbed from salt-free solution).

\[
\frac{F_{DH}(D)}{2\pi R} = 64\frac{k_BT N_A e C}{\kappa} \tanh^2 \left( \frac{e \psi_0}{4k_BT} \right) e^{-\kappa D} = 0.0482 \sqrt{I_{NaCl}} \tanh^2 \left( \frac{\psi_0(mV)}{103} \right) e^{-\kappa D}
\]  
*(6.1)*
\[
\sigma_0 = \sqrt{8 k_B T \varepsilon_0 \varepsilon \rho_{\infty}} \sinh \left( \frac{e \psi_0}{2 k_B T} \right) = 0.117 \sqrt{I_{NaCl}} \sinh \left( \frac{\psi_0 (mV)}{51.5} \right) \tag{6.2}
\]

Upon increase of the ion concentration, the surface potential \(\psi_0\) decreases by a factor of 3 and the surface charge density \(\sigma_0\) increases. These features were often described for charged flat surfaces (Eq. 6.1, Eq. 6.2)

![Figure 6.3](image)

**Figure 6.3:** Comparison between the fitted parameters of the surfaces covered with, (a, b) PDADMA, PEI / PSS / [PDADMA / PSS] \(9\) and (c, d) PEI / PSS / [PDADMA / PSS] \(9\) / PDADMA (physorbed from 100 mM NaCl solution) using the direct force profiles (cf. Fig. 6.1). The surface potential \(\psi_0\) (a, c) of PSS and PDADMA terminated films respectively, are fitted using Eq. 6.1. The surface charge densities \(\sigma_0\) (b, d) of PSS and PDADMA terminated films respectively, are calculated by Grahame’s equation (Eq. 6.2), to the fitted \(\psi_0\).

### 6.1.2 PEI / PSS / [PDADMA / PSS] \(9\) with PSS terminated film

The forces which act between bare silica CP and PEI/PSS / [PDADMA/PSS] \(9\) film (i.e., the number of layer pairs of the polyelectrolyte multilayer film is increased
6.1 Surface forces of PSS terminated polyelectrolyte multilayers

to N = 9) with PSS as a top layer, as a function of surface separation \( D \), were recorded in sequence with increasing NaCl concentrations in water from 0 M to 1 M (cf. Fig. 6.4, top left). Once 3 M was reached, the concentrations were decreased again to 1 and 0.1 mM, then to pure water again (cf. Fig. 6.4, top right).

**Figure 6.4:** Force-distance profiles (dots, obtained by averaging over 150 approach curves) acting between silica CP and PEI / PSS / \([\text{PDADMA/PSS}]_9\) film (physiosorbed from 0.1 M NaCl) with PSS as a top layer. The force curves (FCs) were recorded in sequence with increasing NaCl concentrations in water (arrows) from 0 M to 1 M (top left), then increased to 3 M and then decreased again to 1 and 0.1 mM, then pure water (top right). The FCs were fitted to the linear DLVO theory (solid lines, (Eq. 6.3)) of the electrostatic double layer. Tapping mode images of the dry film were measured in air, before (surface roughness = 1.1 nm, bottom left) and after FC measurements (surface roughness = 4 nm, bottom right). The increase in surface roughness suggests an irreversible rearrangement of the chains due to binding counterions.

These forces are electrostatic and decrease in range with increasing ion concentration as is shown further down. Always the repulsive forces increase exponentially with decreasing surface separation. The repulsive interaction between polyelectrolyte multilayer surface with PSS as a top layer and the similar charged planar silica surface is given by [Block, 2010; Israelachvili, 1991]
Chapter 6  Surface Forces of Polyelectrolyte Multilayers

\[ P_{DH}(D) = 64 k_B T \rho_\infty \tanh \left( \frac{e \psi_{0,\text{SiO}_2}}{4k_B T} \right) \tanh \left( \frac{e \psi_{0,\text{PSS}}}{4k_B T} \right) e^{-\kappa D} \]

\[ \frac{F_{DH}(D)}{2\pi R} = 64 k_B T N_A c \tanh \left( \frac{e \psi_{0,\text{SiO}_2}}{4k_B T} \right) \tanh \left( \frac{e \psi_{0,\text{PSS}}}{4k_B T} \right) e^{-\kappa D} \]

Subsequently, the asymmetric measurements of electrostatic repulsive force acting between bare silica CP and PEI / PSS / [PDADMA / PSS] \(_9\) film with PSS as a top layer was fitted by applying Eq.6.3 to the direct force measurements (c.f. Fig.6.4).

\[ \frac{F_{DH}(D)}{2\pi R} = 0.0482 \sqrt{I_{\text{NaCl}}} \tanh \left( \frac{\psi_{0,\text{SiO}_2}}{103} \right) \tanh \left( \frac{\psi_{0,\text{PSS}}}{103} \right) e^{-\kappa D} \quad (6.3) \]

where \( \psi_{0,\text{SiO}_2} \) and \( \psi_{0,\text{PSS}} \) are the surface potential of the CP silica surface, and the PSS top layer respectively. The surface potential \( \psi_{0,\text{SiO}_2} \) of the silica CP at different salt concentrations (Tab.9.1) is used as a fixed parameter in Eq.6.3 to the fitting data (Fig.6.5, top right). Tapping mode images in air of the dry film before (surface roughness = 1.1 nm) and after FC measurements (surface roughness = 4 nm) are shown in (Fig.6.4, bottom left and right respectively).

The decay length (Fig.6.5, top left) is very similar to the theoretical Debye length \( \kappa^{-1} \) (Fig.6.5, top left (line)) up to an ion concentration of 100 mM. The agreement between calculated Debye length (Eq.3.21) demonstrates that these repulsive forces are of electrostatic origin. By increasing the NaCl concentration more, the top layer PSS reswells again and the decay length increases in a non-electrostatic manner (Fig.6.5, top left). The surface charge density \( \sigma_{0,\text{PSS}} \) of the PSS (Fig.6.5, bottom left) is obtained by applying Grahame’s equation (Eq.6.2) to \( \psi_{0,\text{PSS}} \). As is expected for a PSS terminated film, the surface charge density has a negative sign. For PEI / PSS / [PDADMA / PSS] \(_9\) film with PSS as a top layer, the surface charge density and surface potential (Fig.6.5) are very similar to the values observed by [Block, 2010] for one layer of PSS (physisorbed from salt-free solution) for salt concentration between 1 mM to 100 mM. For ionic strength \( I_{\text{NaCl}} > 100 \) mM it does not make more sense to calculate a surface potential and a surface charge since the forces are non-electrostatic (see Eq.3.21(top left)). It is concluded that the surface is a hard flat surface.
6.1 Surface forces of PSS terminated polyelectrolyte multilayers

Figure 6.5: The fitted parameters of the PEI / PSS / [PDADMA / PSS]_9 film (physisorbed from 0.1 M NaCl). The decay length $\lambda^{-1}$ (top left) and the surface potential, $\psi_{0,\text{PSS}}$ (top right) are fitted by the force-distance profiles Fig. 6.4 and DLVO theory (Eq. 6.3). The fitting parameters of silica CP in (Tab. 9.1) are used to calculate the surface potential of PSS, $\psi_{0,\text{PSS}}$. The decay length (top left) is very similar to the theoretical Debye length $\kappa^{-1}$ (line, (Eq. 3.21)) up to ion concentration of 100 mM. By increasing the NaCl concentration more, the top layer PSS reswells again, and the decay length increases in a non-electrostatic way (top left). The surface charge density $\sigma_{0,\text{PSS}}$ (bottom left) is calculated by applying Grahame’s equation (Eq. 6.2), to the fitted $\psi_{0,\text{PSS}}$.

6.1.3 PEI / PSS / [PDADMA / PSS]_{14} with PSS terminated film

By increasing the number of layer pairs of the polyelectrolyte multilayer film to $N = 14$, strong negative forces act between silica CP covered with PEI / PSS and PEI / PSS / [PDADMA / PSS]_{14} film with PSS terminated film at the water and 0.05 mM were observed. The magnitude of this force decreased by increasing the ionic strength and almost disappeared at 1 mM, and appeared again for salt...
concentrations between 5 mM to 100 mM (Fig. 6.5, top left). This, surprisingly, indicates that the PSS top layer is not negatively charged, but positively charged. The decrease of attractive force indicates decaying surface charge on increase of ion concentration up to 100 mM.

![Figure 6.6](image)

**Figure 6.6:** Force-distance profiles (dots, obtained by averaging over 150 approach curves) acting between silica CP covered with PEI/PSS and PEI / PSS / [PDADMA / PSS]\textsubscript{14} film (physisorbed from 0.1 M NaCl) with PSS as a top layer (left). The FCs recorded in sequence with increasing NaCl concentrations in water (arrows) from 0 to 0.1 M, show adhesion forces, indicating that the top layer PSS is not negatively charged. Force-distance profiles (right, dots) acting between silica CP covered with PEI and PEI / PSS / [PDADMA / PSS]\textsubscript{14} film (physisorbed from 0.1 M NaCl) with PSS as a top layer. The FCs (right) are fitted to the linear DLVO theory (solid lines, (Eq. 6.3)) of the electrostatic double layer to confirm the positive charge of the top layer of the film, and small negative forces appear at 100 mM NaCl concentration. The tapping mode image for the dry film as it is prepared (bottom left, surface roughness = 1.26 nm).

Therefore, the forces act between silica CP covered with the PEI (positively charged) and PEI / PSS / [PDADMA / PSS]\textsubscript{14} film with PSS as a top layer as a function of surface separation D were recorded in sequence with increasing NaCl concentrations.
in water from 0 M to 100 mM (c.f. Fig. 6.5, top right). For this system, electrostatic repulsive forces are observed.

Figure 6.7: The fitted parameters of PEI / PSS / [PDADMA / PSS]_{14} (physisorbed at 0.1 M NaCl). The decay length, $\lambda^{-1}$ (top left) and the surface potential, $\psi_{0,\text{PSS}}$ (top right) are fitted by the force-distance profiles (Fig. 6.6, right) and DLVO theory (Eq. 6.3). The fitting parameters of the PEI surface in Tab. 9.3 are used to calculate the surface potential of PSS, $\psi_{0,\text{PSS}}$. The decay length $\lambda^{-1}$ (top left) is very similar to the theoretical Debye length $\kappa^{-1}$ (line, (Eq. 3.21)) up to ion concentration of 10 mM. At 0.1 M NaCl concentration, the decay length deviates from the theoretical value and shows a small adhesion force at low surface separation. The surface charge density, $\sigma_{0,\text{PSS}}$ (bottom) is calculated by Grahame’s equation (Eq. 6.2), to the fitted, $\psi_{0,\text{PSS}}$.

The repulsive interaction between polyelectrolyte multilayer surface with PSS as a top layer and the different charged CP covered with PEI is given by

$$\frac{F_{DH}(D)}{2\pi R} = 0.0482 \sqrt{I_{NaCl}} \tanh \left( \frac{\psi_{0,\text{PEI}} \text{ (mV)}}{103} \right) \tanh \left( \frac{\psi_{0,\text{PSS}} \text{ (mV)}}{103} \right) e^{-\kappa D} \quad (6.4)$$
where $\psi_{0,\text{PEI}}$ and $\psi_{0,\text{PSS}}$ are the surface potential of the CP covered with PEI, and the PSS top layer of polyelectrolyte multilayer film respectively. The surface potential $\psi_{0,\text{PEI}}$ of the CP covered with PEI at different salt concentration (Tab.9.3) is used as a fixed parameter in Eq.6.4 to the fitting data (Fig.6.7, top right). Tapping mode images of the dry film are measured in air before FC measurements show a surface roughness of 1.26 nm as it is found in Fig.6.6 (bottom left).

Similar to $N = 9$, the decay length at $N = 14$ (Fig.6.7, top left) is very similar to the theoretical Debye length $\kappa^{-1}$ (cf. Fig.6.7, top left (line)) up to ion concentration of 10 mM. At 0.1 M NaCl concentration the decay length deviates from the theoretical value and shows small adhesion force at low surface separation. The surface charge density $\sigma_{0,\text{PSS}}$ of the PSS film is obtained by applying Grahame’s equation (Eq.6.2) to $\psi_{0,\text{PSS}}$. Surprisingly, the surface charge density of the PSS terminated film has a positive sign (cf. Fig.5.7 (bottom)). At $I_{NaCl} = 100$ mM the decay length is shorter than predicted by DLVO theory. Therefore, we conclude that the surface is neutral and the repulsive force is hard-core repulsion.

### 6.1.4 PEI / PSS / [PDADMA / PSS]$_{19}$ with PSS terminated film

For the polyelectrolyte multilayer film with $N = 17$ and 19, repulsive forces act between silica CP covered with PEI (positively charged) and PEI / PSS / [PDADMA / PSS]$_{17,19}$ film with PSS as a top layer as a function of surface separation $D$. Small adhesive force is observed at 100 mM for $N = 17$ (cf. Fig.6.8, top left) and at 50 mM, and 100 mM for $N = 19$ (cf. Fig.6.8, top left). For PEI / PSS / [PDADMA / PSS]$_{19}$ film with PSS as a top layer, the top layer PSS starts to reswell at 1-4 M and the forces get more long-ranged by washing the NaCl away with water (cf. Fig.6.8, top right). The tapping mode images of the dry film show a surface roughness of 1.43 nm in air before (see Fig.6.8, bottom left) FC measurements, and surface roughness of 2.6 nm after (see Fig.6.8, bottom right). The increase of surface roughness suggests irreversible rearrangement of the chains due to binding counterions. The FCs in Fig.6.8 are fitted again to the linear DLVO theory (cf. Eq.6.4) of the electrostatic double layer at constant potential approximation. The surface potential $\psi_{0,\text{PEI}}$ of the CP covered with PEI at different salt concentrations (see Tab.9.3) is used as a fixed parameter in Eq.6.4 to the fitting data (cf. Fig.6.8, top left). At $N = 14, 17, 19$, the surface potential $\psi_{0,\text{PSS}}$ and the surface charge density $\sigma_{0,\text{PSS}}$ of PSS as the top layer are very similar and all show a positive sign. The PSS surface is neutral at 100 mM (preparation concentration). The comparison between the surface charge density $\sigma_{0,\text{PSS}}$ of PEI / PSS / [PDADMA / PSS]$_N$ films
6.1 Surface forces of PSS terminated polyelectrolyte multilayers

(N = 1, 9, 14, 17, 19) terminated with PSS is shown in Fig. 6.10. For layer pairs numbers N = 1, 9 the film surface is negatively charged (cf. Fig. 6.10, blue) and for N = 14, 17 and 19 the film surface is positively charged (dark blue). No surface charge could be detected at 0.1 M NaCl for N = 1, 14, 17, and 19. Additionally, no surface charge was found at 0.05 M NaCl for N = 19, and at 1 M NaCl for N = 14, respectively. All fitting parameters of PSS terminated surface for N = 9, 14, 17, and 19 are shown in Tab. 6.1.

Figure 6.8: Force-distance profiles (dots, obtained by averaging over 150 approach curves) acting between silica CP covered with PEI and PEI / PSS / [PDADMA / PSS]_{19} film (physisorbed from 0.1 M NaCl) with PSS as a top layer. The FCs were recorded in sequence with increasing NaCl concentrations in water (arrows) from 0 M to 0.01 M (top left). At 0.05 M and 0.1 M, adhesion forces appeared indicating a small collapse (top right). At 1 M, the top layer PSS starts to reswell again, until 4 M, and collapses when 4 M NaCl solution is replaced with salt-free water (top right). A brush is no longer found. The electrostatic FCs are fitted to the linear DLVO theory (solid lines, (Eq. 6.3)) of the electrostatic double layer at constant potential approximation. Tapping mode images of the dry film were measured in air before (bottom left, surface roughness = 1.43 nm) and after FC measurements (surface roughness = 2.6 nm, bottom right). The increase in surface roughness suggests irreversible rearrangement of the chains due to binding counterions.
Figure 6.9: The fitted parameters of PEI / PSS / [PDADMA / PSS]_{19} film (physisorbed from 0.1 M NaCl). The decay length, $\lambda^{-1}$ (top left) and surface potential, $\psi_{\text{PS}}$ (top right) are fitted by DLVO theory (Eq. 6.3) to the repulsive force-distance profiles (cf. Fig. 6.8, left). The parameters of PEI surface in Tab. 9.3 are used. Decay length at 0-10 mM NaCl concentration (top left, solid line) indicate that the PSS top layer of the multilayer film is adsorbed flatly. At 0.05 and 0.1 M NaCl concentration the decay length deviates from the theoretical value, and shows that the surface is neutral and from 1 M to 4 M the top layer PSS starts to reswell in a non-electrostatic way (top left). The surface charge density, $\sigma_{\text{PS}}$ (bottom), with a positive sign for the electrostatic forces is calculated by applying Grahame’s equation (Eq. 6.2), to the fitted $\psi_{\text{PS}}$. 
Figure 6.10: A comparison between the surface charge density $\sigma_{0,\text{PSS}}$ of PEI / PSS / [PDADMA / PSS]_N films (N = 1, 9, 14, 17, 19) terminated with PSS. For layer pair numbers $N = 1, 9$ the film surface is negatively charged (blue) and for $N = 14, 17$ and 19 the film surface is positively charged (dark blue). The PSS surface started to be neutral at 0.1 M NaCl for $N = 1, 14, 17$, at 0.05 M NaCl for $N = 19$, and at 1 M NaCl for $N = 14$, respectively.
Table 6.1: Linearized Poisson-Boltzmann (PB) model parameters obtained from fitting the FCs measurements. The electrostatic parameters fitted according to (Eq.9.1) to get the decay length and the surface potential of PSS. The surface charge density \(\rho_0\) is obtained by applying Grahame's equation, \(\rho \approx \frac{\rho_0}{\gamma_{\text{PEI}}}\). The surface charge density \(\sigma_0\) of PSS as obtained by applying Grahame's equation, \(\sigma \approx \frac{\rho_0}{\gamma_{\text{PEI}}}\).

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6.2 Tuning the surface forces of PDADMA terminated polyelectrolyte multilayers

To study the effect of changing N of polyelectrolyte multilayer film with PDADMA as a top layer, the force-distance profiles between a CP and PDADMA terminated surface with different N were measured. In this part, N = 9, 14, 17, 19 of polyelectrolyte multilayer film are introduced with PDADMA as a top layer. The theory of Alexander and de Gennes (AdG) is used to fit the force-distance profiles. The theory of AdG provides a simple model to explain steric interaction with two free parameters. The AdG force profile of symmetric and asymmetric cases are given respectively by

\[
W_{AdG,symm}(D) = \frac{F_{AdG,symm}(D)}{2\pi R} = \frac{8k_BT L}{35s^3} \left[ 7 \left( \frac{D}{2L} \right)^{-\frac{3}{2}} + 5 \left( \frac{D}{2L} \right)^{\frac{7}{2}} - 12 \right] \quad (6.5)
\]

\[
W_{AdG,asymm}(D) = \frac{F_{AdG,asymm}(D)}{2\pi R} = \frac{2k_BT L}{35s^3} \left[ 7 \left( \frac{D}{L} \right)^{-\frac{3}{2}} + 5 \left( \frac{D}{L} \right)^{\frac{7}{2}} - 12 \right] \quad (6.6)
\]

where \( L \) is the brush thickness, and \( s \) is the average distance between two grafting points of the brushes, respectively. The force profiles are non-linear functions and they are approximated at intermediate surface separations (0.2 \( \leq D/L \leq 0.9 \)) by an exponential function with a decay length given by \( \gamma^{-1} = -L/\pi \) (symmetric) and \( \gamma^{-1} = -L/2\pi \) (asymmetric), respectively [Israelachvili, 1991]. The apparent surface separation \( D_{CP} \) refers to the surface separation at the contact point of both interacting polyelectrolyte layers. The contact is reached if the displacements of the cantilever and piezo are equal (constant compliance). However, the definition of \( D \) in Eq.6.5 is the real distance between the substrate surfaces. The polyelectrolyte layers can only be compressed to a height \( \delta \), before both substrates touch each other and squeeze the polyelectrolyte out of the contact area leading to unreproducible approach/separation measurements. The relation between the true \( D \) and the apparent surface separation \( D_{CP} \) is given by \( D = D_{CP} + \delta \). It is important to determine this displacement \( \delta \) as the fitting value of the grafting density \( s \) depends on it [Block, 2010]. To perform the AdG fit to force profiles using Eq. 6.5 and Eq. 6.6, a first estimation for the brush thickness \( L \) should be obtained. As the AdG force profile decays exponentially at surface separations in the range of 0.2 \( \leq D/L \leq 0.9 \), the measured force profile is fitted by an exponentially decaying function and
$\gamma^{-1} = -L/2\pi$ (asymmetric) [Israelachvili, 1991] are used as a first approximation. This first estimation of $L$ is used to start a least mean squares (LMS) fit of Eq. 6.6 to the force profile. The free parameters $L$, $s$ and $\delta$ are optimized to scope a good fit using Eq. 6.6 to the measured force profile in the asymmetric case [Block, 2010].

### 6.2.1 PEI / PSS / [PDADMA / PSS]$_9$ with PDADMA terminated film

![Force-distance profiles acting between silica CP covered with PEI and PEI / PSS/ [PDADMA / PSS]$_9$/ PDADMA film (physisorbed from 0.1 M NaCl) with PDADMA as a top layer. The force curves were recorded while the salt concentration (arrows) was increased consecutively from 0 M to 0.1 M (top left). At ionic strength between 1 and 3 M attraction attributed to bridging forces is observed (top right). The PDADMA top layer reswells again by decreasing the salt concentration to 1 mM and water, respectively (top right). The FCs are fitted to the AdG theory for the asymmetric case (solid lines, Eq.6.6). The tapping mode images for the dry film were measured in the air before (bottom left, surface roughness = 0.78 nm) and after FC measurements (surface roughness = 1.38 nm, bottom right).](image-url)

**Figure 6.11:** Force-distance profiles (dots, obtained by averaging over 150 approach curves) acting between silica CP covered with PEI and PEI / PSS/ [PDADMA / PSS]$_9$/ PDADMA film (physisorbed from 0.1 M NaCl) with PDADMA as a top layer. The force curves were recorded while the salt concentration (arrows) was increased consecutively from 0 M to 0.1 M (top left). At ionic strength between 1 and 3 M attraction attributed to bridging forces is observed (top right). The PDADMA top layer reswells again by decreasing the salt concentration to 1 mM and water, respectively (top right). The FCs are fitted to the AdG theory for the asymmetric case (solid lines, Eq.6.6). The tapping mode images for the dry film were measured in the air before (bottom left, surface roughness = 0.78 nm) and after FC measurements (surface roughness = 1.38 nm, bottom right).
Fig. 6.11 displays force-distance profiles (averaging over 150 approach curves) acting between silica CP covered with PEI and PEI / PSS / [PDADMA / PSS]_9 / PDADMA film (physisorbed from 0.1 M NaCl) with PDADMA as a top layer. The force curves were recorded while the salt concentration was increased consecutively from 0 M to 3 M, and reduced again to 1 mM and water, respectively. All repulsive force profiles were fitted by an exponentially decaying equation, as it is described in Sec. 6.1. The decay lengths $\lambda^{-1}$ found by this fitting are introduced in Fig. 6.17 (red, N = 9), and the line gives the theoretical Debye length $\kappa^{-1}$. This figure clearly shows that $\lambda^{-1}$ strongly differs from the Debye length and does not show $1/\sqrt{I_{NaCl}}$ scaling of the Debye length. Clearly, this cannot be described by the Poisson-Boltzmann-theory. The measured forces cannot be explained using the electrostatic double layer repulsion approximation. The high values of decay length and the long range of the measured forces bring us to conclude that some parts of the polyelectrolyte dangle into the solution and the polyelectrolyte layer shows a non-flat conformation. By taking these considerations, it is reasonable to use the steric theory to explain polyelectrolyte brush conformation. The FCs are fitted to AdG theory for the asymmetric case (Fig. 6.11 (left, lines), Eq. 6.6). The surface roughness of the dry film was performed in air using the AFM tapping mode and it shows 0.78 nm before (Fig. 6.11, bottom left) and 1.38 nm after (see Fig. 6.11, bottom right) FC measurements. The PDADMA brush thickness $L$ is plotted as a function of the product of molecular area $s^2$ and ionic strength $I_{NaCl}$ in Fig. 6.12 (left). By increasing the ionic strength $I_{NaCl}$, the brush length $L$ shrinks (Fig. 6.12, bottom). The regression line obtained by a LMS-fit to the data points is shown in Fig. 6.12 (bottom), which also shows that the data points at an ionic strength between 0 M and 0.01 M follow the power law of the form $L \propto (I_{NaCl} \cdot s^2)^\alpha$. The slope of the regression line equals $\alpha = -0.22$ and confirms that the PDADMA top layer shows a brush-like conformation. The brush thickness exceeds 150 nm for most ionic strengths, which is 22% of the PDADMA contour length. A strong decrease in $L$ with an increase in the ionic strength to 0.05 M and 0.1 M, and a collapse of the brush layer are observed. At high ionic strength between 1 M and 3 M, dramatic shrinking and negative bridging forces are found. However, a reswelling happens when the ionic strength is decreased again to 1 mM and water (cf. Fig. 6.11, top right). Furthermore, the average chain distance $s$ (cf. Fig. 6.12, right) is constant during the measurement.
Figure 6.12: Steric parameters obtained from the AdG theory to the force profiles (Fig. 6.11, top left). The average distance $s$ between the pseudo-tails is almost constant during an increase in salt concentration in measurements with a small deviation at 0.5 and 0.1 M (left) when the brush collapses. The top layer PDADMA swells, shrinks, and reswells reversibly and the brush thickness corresponding to 20% of the PDADMA contour length is observed at $I_{NaCl} = 1$ mM (right), which indicates that part of the PDADMA chains protrude into solution and the rest build a complex with the PSS chain inside the multilayer film.
6.2 Tuning the surface forces of PDADMA terminated polyelectrolyte multilayers

6.2.2 PEI / PSS / [PDADMA / PSS]14 with PDADMA terminated film

Figure 6.13: Force-distance profiles (dots, obtained by averaging over 150 approach curves) acting between silica CP covered with PEI / PDADMA / PSS and PEI / PSS / [PDADMA / PSS]14 film (physisorbed from 0.1 M NaCl) with PDADMA as a top layer. The FCs recorded in sequence with increasing NaCl concentrations in water (arrows) from 0 M to 1 M (left). The FCs are fitted to AdG theory for the asymmetric case ((top left, solid lines), Eq.6.6). The tapping mode image for the dry film in air shows surface roughness = 1.63 nm (right).

In this part, N = 14 of polyelectrolyte multilayer film with PDADMA as a top layer is introduced. The force-distance profiles (cf. Fig.6.13, dots), acting between silica CP covered with PEI / PDADMA / PSS and PEI / PSS / [PDADMA / PSS]14 films (physisorbed from 0.1 M NaCl), with PDADMA as a top layer. The FCs are fitted to AdG theory for the asymmetric case (cf. Fig.6.13 (left, lines), Eq.6.6). As it is observed in the previous part, the polyelectrolyte multilayer film with PDADMA terminated surface also shows here a brush-like conformation. The PDADMA brush thickness $L$ is shown as a function of $s^2$ and ionic strength $I_{NaCl}$ in Fig.6.14 (left). By increasing the ionic strength $I_{NaCl}$, the brush length $L$ shrinks (cf. Fig.6.12, bottom). The regression line obtained by a LMS-fit to the data points is shown in Fig.6.12, which also shows that the data points at an ionic strength between 0 M and 0.05 M follow the power law of the form $L \propto (I_{NaCl} \cdot s^2)^\alpha$. The slope of the regression line equals $\alpha = -0.16$. A decrease of $L$ with increases in the ionic strength to 0.1 M, and a collapse of the brush layer is observed. At high ionic strength of 1 M a slight reswelling of the brush takes place. Again, the average chain distance $s$ (cf. Fig.6.14, right) appears to be constant during the measurement.
Figure 6.14: Steric parameters obtained by the AdG theory to the force profiles (Fig. 6.13, top left). The average distance $s$ between the pseudo-tails is almost constant during salt increase in measurements with a small decrease at 0.5 and 0.1 M when the brush collapses (top left). The top layer PDADMA swells, shrinks, and reswells reversibly with salt addition (bottom) and the brush thickness corresponding to 15-20% of the contour length is observed at $I_{NaCl} = 1$ mM (top right), which indicates that part of the PDADMA chains protruding into solution and the rest of the PDADMA chains build complexes with PSS chains inside the multilayer film.
6.2 Tuning the surface forces of PDADMA terminated polyelectrolyte multilayers

6.2.3 PEI / PSS / [PDADMA / PSS]$_{19}$ with PDADMA terminated film

Figure 6.15: Force-distance profiles (dots, obtained by averaging over 150 approach curves) acting between silica CP covered with PEI and PEI/PSS/[PDADMA/PSS]$_{19}$ film (physisorbed from 0.1 M NaCl), with PDADMA as a top layer. The FCs were recorded with increasing NaCl concentration in water (arrows) from 0 M to 0.1 M (top left). At ionic strength between 1M and 4 M, reswelling of the chains was observed (top right). The PDADMA top layer reswells less by decreasing the salt concentration to 1 mM and water respectively (top right). The FCs are fitted to AdG theory for the asymmetric case (solid lines, Eq.6.6). Tapping mode images in air of the dry film before (bottom left, surface roughness = 2.1 nm) FC measurements. The surface contaminated during the sample cutting process.

Here, $N = 19$ of polyelectrolyte multilayer film with PDADMA as a top layer is introduced. The force-distance profiles (cf. Fig.6.15, dots) acting between silica CP covered with PEI and PEI / PSS / [PDADMA / PSS]$_{19}$ film (physisorbed from 0.1 M NaCl) with PDADMA as a top layer. The FCs are fitted to AdG theory for the asymmetric case (Fig.6.15 (left, lines), Eq.6.6).
Figure 6.16: Steric parameters obtained by fits to the AdG theory from the force profiles shown in Fig. 6.15. The average distance $s$ between the pseudo-tails is almost constant during increase of the salt concentration (left). The top layer PDADMA swells, shrinks, and reswells reversibly and the brush thickness corresponding to 20% of the contour length is observed at $I_{NaCl} = 1$ mM (right) which indicates that part of the PDADMA chains protrude into solution and the rest builds a complex with PSS chains inside the multilayer film. An unexpected strong reswelling behaviour is observed at 1 to 4 M NaCl.

As it is observed in the previous part, the polyelectrolyte multilayer film with PDADMA terminated film always shows a brush-like conformation. The PDADMA brush thickness $L$ as a function of $s^2$ and ionic strength $I_{NaCl}$ in Fig. 6.14 (left). By increasing the ionic strength $I_{NaCl}$, the brush length $L$ shrinks (cf. Fig. 6.12, bottom). The regression line obtained by a LMS-fit to the data points is shown in the figure, which shows also that the data points at an ionic strength between 0 M and 0.01 M follow the power law of the form $L \propto (I_{NaCl} \cdot s^2)^\alpha$. The slope of the regression line equals $\alpha = -0.2$. A decrease of $L$ with increase the ionic strength to 0.05 M and 0.1 M and a collapse of the brush layer is observed. At high ionic strength of 1 M to 4 M a reswelling of the brush takes place. Again, the average
6.2 Tuning the surface forces of PDADMA terminated polyelectrolyte multilayers

The chain distance $s$ (see Fig. 6.14, right) seems to be constant during the measurement. The surface roughness of the dry film in air is measured using the AFM tapping mode and it shows 2.1 nm before (cf. Fig. 6.15, bottom left) and 0.88 nm after (Fig. 6.15, bottom right) FC measurements.

**Figure 6.17:** A comparison between the decay length $\lambda^{-1}$ of PEI / PSS / [PDADMA/PSS]$_N$ multilayer films ($N = 9, 14, 17, 19$) with PSS terminated (blue) and PDADMA terminated (red) as a function of the salt concentration. PDADMA terminated films have a brush conformation and the decay length decreases with increasing salt concentration (collapse) and at 1 M the PDADMA top layer reswells again for $N = 19$. The PSS terminated films show flat conformation all the time, but reswell for $N = 10, 19$.

Fig. 6.17 compares the decay length $\lambda^{-1}$ of the polyelectrolyte multilayer film of PSS and PDADMA terminated films. PSS terminated films show a flat conformation at an ionic strength $< 0.1$ M (Fig. 6.17, blue) with a negative charge sign at $N \leq 9$. The reswelling of the PSS chain takes place at high ionic strength of 1 M to 3 M. The surface charge of PSS turns to a positive sign at $N > 9$ (Fig. 6.17, dark blue). For PDADMA terminated films, the decay length does not show any agreement with the electrostatic Debye length (see Fig. 6.17, red). At ionic strength $< 0.1$ M, steric forces act between the chains and the brush protrudes in the solution. The chains collapse and show bridging forces at high ionic strength of 1 M to 4 M for $N = 9$. For the $N$ equal to 14, 17 and 19 and by increasing the ionic strength of 1 M to 4 M, the brush thickness increases. At this reswelling effect, the chains behave
as polymers brushes. All fitting parameters of PDADMA terminated film for $N = 9, 14, 17,$ and 19 are shown in Tab. 6.2.
6.2 Tuning the surface forces of PDADMA terminated polyelectrolyte multilayers

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Table 6.2: The fitting parameters of AdG theory applied to the asymmetric force measurements of PEI / PSS / [PDADMA/PSS]$_N$ / PDADMA films (N = 9, 14, 17 and 19) with PDADMA as a top layer (physisorbed from 0.1 M NaCl).
6.2.4 Discussion

For asymmetric force measurements of polyelectrolyte multilayer films with a PSS top layer, physisorbed from 0.1 M NaCl, the surface charge of PSS depends on the number of PSS / PDADMA layer pairs N. PSS always shows a flat conformation as a top layer of the multilayer film, physisorbed from 0.1 M NaCl. The surface charge of PSS is negative for N < 14. At N = 14, the surface charge is positive. By increasing N to 17, 19, PSS stays positive. A similar effect was also found by [Ghostine et al., 2013; Arias et al., 2016], which concludes that at a specific number of layer pairs, slight negative charges were found on the PSS surface. A similar surface was also tested by protein adsorption (albumin, negatively charged) [Salloum and Schlenoff, 2004; Dizge et al., 2018]. The PSS terminated film, at a high number of layer pairs, adsorbs a very small amount of negative protein. It is pointed out in [Ghostine et al., 2013] that at the start of a linear growth regime (correlated with layer pair number), positive extrinsic sites start to accumulate within the PSS terminated film. Because of this accumulation of the positive extrinsic sites within the PSS layer, the surface charge of the PSS at N ≥ 14, 17, 19 shows a positive sign. At an ionic strength equal to 0.1 M (the preparation concentration), the PSS top layer collapses and a neutral or zwitterionic surface is formed. Commonly, at this high ionic strength, exponentially decaying hydration forces with decay length \( \lambda^{-1} \approx 0.1 \text{ nm} \) are observed [Israelachvili, 1991]. Therefore, the measured forces at ionic strength \( \approx 0.1 \text{ M} \) for terminated PSS are evidence of hydration forces with unusual long-ranged decay length \( \lambda^{-1} \approx 0.2-0.5 \text{ nm} \). For ionic strength > 0.1 M, the PSS top layer reswells in the solution. The reason for this was explained by Mei and Ballauff to be the adsorption of salt ions in the polyelectrolyte chain [Mei and Ballauff, 2005]. This adsorption leads to an increase in the size of the segments [Mei and Ballauff, 2005]. A reswelling of the PSS top layer after collapse at 0.1 M NaCl follows this. An alternating exposure of a substrate to the monomer of the polyanion and polycation is the main assembling cause of a polyelectrolyte multilayer film [Schlenoff et al., 1998]. A polyanion monomer is symbolized by Pol\(^-\) and a polycation monomer by Pol\(^+\) [Fares and Schlenoff, 2017]. The surface charge of the PSS layers is determined by equilibrium according to the law of mass action where the amount of monomers at the surface is constant:

\[
[\text{Pol}^- \ \text{Pol}^+] + [\text{Pol}^+ \ \text{Cl}^-] + [\text{Pol}^- \ \text{Na}^+] + [\text{Pol}^+] + [\text{Pol}^-] = \text{const}.
\]

At low [Na\(^+\)] and [Cl\(^-\)], less ions are bound on the surface, and [Pol\(^+\)] and [Pol\(^-\)] are increased. Depending on the composition of the surface, the film is positively or
negatively charged. If $[\text{Na}^+]$ and $[\text{Cl}^-]$ are increased beyond 0.1 M, then $[\text{Pol}^- \text{Na}^+]$ and $[\text{Pol}^+ \text{Cl}^-]$ increase and more ions are bound to the chains. At the same time, less ionic monomer-monomer bonds ($[\text{Pol}^- \text{Pol}^+]$) are found at the surface. Therefore, some chain fractions are no longer attached to the film but dangle into solution (reswelling).

In addition, for asymmetric force measurements of polyelectrolyte multilayer films with PDADMA terminated surface physisorbed from 0.1 M NaCl, the behaviour of PDADMA chains depends on the number of layer pairs. For one and 5 polyelectrolyte layers, the PDADMA shows a flat conformation and the reason for this is the strong monomer-monomer interaction. By increasing $N$ to 9, 14, 17, 19, PDADMA behaves like a salted polyelectrolyte brush. The thickness of the pseudo-brush scales, as known for salted polyelectrolyte brushes, and dramatic changes in the brush thickness are observed when increasing and decreasing the ionic strength. Interestingly, the force profiles are well explained using the theory of Alexander and de Gennes, which was found to explain neutral end-grafted polymers [Alexander, 1977; de Gennes, 1987]. The PDADMA terminated film has been described as veritable sponges for protein adsorption [Salloum and Schlenoff, 2004]. It was also observed in [Iturri Ramos et al., 2010] that PEM with PDADMA terminated films are much more hydrated and swollen than the PSS terminated one.

At the number of PDADMA/PSS layer pairs, $N$ increases up to 9 and we can divide the behaviour of PDADMA into three regimes: the first at the low ionic strength and the second at high ionic strength. In the first regime, the brush thickness decreases by increasing the ionic strength, where the steric force between the polyelectrolyte chains dominates ($I_{\text{NaCl}} < 0.1$ M). By increasing the ionic strength ($I_{\text{NaCl}} < 0.1$ M), the imbalance between the counter ion concentration in the brush and in the subphase decreases, therefore the osmotic pressure is reduced and the brush length $L$ shrinks [Ahrens et al., 1998; Zhulina et al., 1995; Block and Helm, 2008]. As a salted brush is formed, the brush thickness $L$ is proportional to $L \propto (I_{\text{NaCl}} \cdot s^2)^{\alpha}$, with the theoretical scaling exponent $\alpha = -1/3$. The brush thickness exceeds 450 nm (in pure water) which is more than 45% of the PDADMA contour length. This strong stretching is not measured for brushes from neutral polymers [Israelachvili, 1991], but for polyelectrolyte brushes [Ahrens et al., 1998]. This can be explained by a strong osmotic pressure produced by counterions that are incorporated into the brush to reach local electro-neutrality in the chain [Block, 2010]. At the second regime ($I_{\text{NaCl}} \approx 0.1$ M), a strong decrease of the brush thickness $L$ and a collapse, and small negative force on the chain are observed. At the third regime ($I_{\text{NaCl}} > 0.1$ M), a short attraction force is observed. To find its origin, further experiments are necessary. As the number of PDADMA/PSS layer pairs $N$ equals 17, and 19, the
Chapter 6 Surface Forces of Polyelectrolyte Multilayers

The behaviour of PDADMA can be divided again into three regimes, the first is at the low ionic strength ($I_{NaCl} < 0.1$ M), which is identical to what happened at $N = 9$. At the second regime ($I_{NaCl} \approx 0.1$ M), flat, neutral or zwitterionic surface is observed ($\lambda^{-1} \approx 0.3-0.9$ nm). The third regime happens at the high ionic strength $I_{NaCl} > 0.1$ M. At this regime, a reswelling effect takes place with an increase in ionic strength, i.e., the brush thickness $L$ increases again and the grafting density is manipulated. This cannot be driven by electrostatic interaction; it is more similar to the polymer brushes. This points to the adsorption of salt ions onto the polyelectrolyte chain. This adsorption leads to an increase in the size of the segments. This is followed by a reswelling of the PDADMA top layer [Mei and Ballauff, 2005].

6.2.5 Conclusion

The surface forces of PSS terminated PEM films have been investigated. Force-distance measurements have been performed at different ionic strength. Always, PSS terminated films show at ionic strength $< 0.1$ M a flat conformation. Because of the positive extrinsic site accumulation within the PSS terminated film, the surface charge of the PSS top layer starts to turn from negative to positive at a number of PDADMA/PSS layer pairs $N \geq 14$. At ionic strength $I_{NaCl} = 0.1$ M, the PSS surface is neutral or zwitterionic and shows unusual long-ranged hydration forces. At ionic strength $> 0.1$ M, the salt ions are adsorbed into the PSS chains, therefore less ionic monomer-monomer bonds are bound to the surface and the chains reswell into the solution.

Complementary, the surface forces of PDADMA terminated PEM films have been performed. At a small number of layers, PDADMA acts similar to PSS and shows flat conformation. For $N = 9, 14, 17, 19$ and ionic strength $\leq 0.1$ M, steric forces are measured. The force-distance profiles are well explained by Alexander and de Gennes theory for neutral end-grafted polymers. PDADMA chains show a maximum brush length around 45% of the contour length. For $N = 9$ and ionic strength $\geq 0.1$ M, a strong screening of electrostatic interaction and attractive force is observed. For ionic strength $I_{NaCl} \approx 0.1$ M, and flat, neutral or zwitterionic surface with a decay length $\lambda^{-1} \approx 0.3 - 0.9$ nm are found. For $N > 9$ and ionic strength $> 0.1$ M, the ions adsorb into the polyelectrolyte chains, which lead to increases in the monomer size, and as a result, the brush thickness $L$ increases and PDADMA brushes protrude again into the solution with different of grafting density. PSS and PDADMA terminated films show this ion adsorption into the chains (reswelling), but for PSS this effect starts earlier with $N = 9$ compared to PDADMA. Therefore we can conclude that surface forces depend very strongly on NaCl concentration in
6.2 Tuning the surface forces of PDADMA terminated polyelectrolyte multilayers solution, and on the number of layer pairs.
7 PEI Layers Physisorbed in the Presence of Iron Ions and Iron Chelate

Here we investigate a branched polyelectrolyte adsorbed from solutions containing divalent ions of the same charge. They interact more specifically with polyelectrolytes than monovalent ions. We chose branched polyethylenimine (PEI) as polycation and Fe$^{2+}$ as a divalent ion. Similar to hemoglobin or ferritin, PEI interacts with Fe$^{2+}$ ions via cooperative bonds. These cooperative bonds stabilize a coiled conformation of PEI [Zhou et al., 1994; Zhu et al., 2006]. To explore the effect of a large oppositely charged divalent ion on PEI, Fe$^{2+}$ was complexed by EDTA. The multivalent anion EDTA stabilizes the coiled conformation of PEI by electrostatic bonds [Juang and Chen, 1996]. The diameter of Fe(EDTA)$^{2-}$ is 0.66-0.82 nm, [Apparent and molar heat capacities and volumes of aqueous chelating agents: ethylendiaminetetraacetic acid EDTA and NDA; Zhonging Wang, Graduate thesis Memorial University New Foundland 1998, page 126] which needs to adopt a suitable conformation to bind two charged PEI segments.

7.1 Material and methods

Materials: Branched polycation poly(ethyleneimine) (PEI; $M_w$= 750 kDa and PDI = 12.5) 50 wt.% in water was purchased from Sigma Aldrich (München, Germany). The iron(II) sulfate heptahydrate (FeSO$_4$) were purchased from Sigma-Aldrich (Steinheim, Germany). EDTA disodium-salt dihydrate was purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany), and sodium chloride from Merck KGaA (Darmstadt, Germany). The concentration of PEI in the adsorption solution for surface functionalization was always 2 mM with respect to the monomer concentration. Negatively charged colloidal gold nanoparticles (AuNPs) synthesized according to [Turkevich, 1951] (diameter ca. 16 nm, AuNPs concentration 2.4 nM
and Debye length 3.89 nm) were used as marker particles. All chemicals were of analytical grade and were used without further purification.

**UV-vis absorption** experiments were performed with a Lambda 900 spectrometer (Perkin-Elmer, U.S.A.). Quartz cuvettes from Hellma Analytics (the light path is 10 mm) were used. Microscope slides (8 x 38 x 1 mm, Menzel (Braunschweig, Germany)) were used.

**Surface preparation.** Oxidized silicon wafers were used for the surface adsorption to perform X-ray reflectivity and force-distance measurements, cleaned according to the RCA standard, and freshly used. Colloidal probes were created by gluing silica spheres (diameter R = 5-6 µm, determined with optical microscopy; purchased from Bangs Laboratories, Fishers, IN) onto tipless cantilevers (CSC12, MicroMash, Tallinn, Estonia) using a UV curable epoxy (NOA68, Norland Adhesives, Cranbury, NJ, U.S.A.). The spring constant \( k = 0.014-0.06 \text{ N m}^{-1} \) was measured separately for every cantilever using the noise spectral density profiles and cleaned with argon-plasma at 35 W for 5 min (Harrick Scientific, NY, U.S.A.) directly before the force measurements. For AFM imaging OMCL-AC160TS cantilevers (spring constant \( k = 42 \text{ N m}^{-1} \)) from Olympus Corporation (Hamburg, Germany) were used. The pH value was measured for salt-free 2 mM PEI (pH = 9.3), 2 mM PEI + 2 mM FeSO₄ (pH = 4.67), and 2 mM PEI + 4 mM FeSO₄ + 5 mM EDTA (pH = 3) solutions at 21 °C before surface coating. For 2 mM PEI solution at pH = 3.2, HCl (Sigma-Aldrich) was used to adjust the pH.

The surfaces were coated with PEI by physisorption for 1 h. After adsorption, the surfaces were directly transferred (i.e., without drying) into the fluid cell of a commercial DI Multimode AFM with a Nanoscope IIIa Controller (Santa Barbara, CA, U.S.A.).

For X-ray reflectivity measurements, Si wafers (Cemat Silicon S.A., Warsaw, Poland) were used as substrates. Cleaning and surface functionalization were as described above. Then, the surfaces were dried either at ambient conditions (approximately 25% r.h.) or with a gentle flow of nitrogen.

**Force Measurements.** The force measurements were performed in PEI-free NaCl solutions of different ionic strengths: starting at salt-free water, then enriching up to 1 M, and diluting again. Force curves were recorded not later than five minutes after change of the solution. Symmetric measurements were performed with both surfaces covered with PEI physisorbed from the same adsorption solution. During one experiment, each salt concentration was recorded at 100–150 force curves at three different positions on the surface, with one approach/separation cycle per five seconds. Shown are only the averaged force curves. In AFM force measurements the
surface separation $D$ is determined from the point of contact of both surfaces, which is the contact of both PE layers in this case. Contact is reached if the displacements of cantilever and piezo are equal (called constant compliance). At this separation, $D = 0$. Afterward, the spring constants were determined using the methods of Butt, Sader, and Cleveland [Cleveland et al., 1993; Butt and Jaschke, 1995; Sader et al., 1999] as described before [Block and Helm, 2008].

**X-ray reflectivity** experiments were performed with a Seifert XRD 3003 TT diffractometer (Seifert, Germany) using Cu Kα radiation (wavelength $\lambda = 1.54$ Å). X-ray reflectivity measurements were performed at nominal 0% rh (relative humidity). The film was placed into a gas tight enclosure (for X-rays: THC, temperature–humidity chamber, Anton Paar GmbH, Graz, Austria) containing a Petri dish filled with P$_2$O$_5$ (Merck, Darmstadt, Germany). X-ray reflection curves provide information about the electron density variation perpendicular to the surface [De Bergevin, 1999]. However, during conventional reflectivity measurements the phase information is lost, and hence, the analysis of the reflectivity data is based on finding a suitable electron density profile of the film. The film is modelled by a series of homogeneous slabs (each slab is parameterized by the total film thickness $l_{slab}$, an interfacial roughness $\sigma_{slab}$, and an electron density $\rho_{slab}$, where the first slab is situated on a silicon substrate with a certain roughness $\sigma_{sub}$ and electron density $\rho_{sub}$. Using the Parratt algorithm [Parratt, 1954], it is possible to calculate the exact X-ray reflection curve for each experiment. Hence, the model parameters for each sample can be obtained by performing a root-mean-square (rms) fit of the calculated reflection curves to the measured data. The detailed model is given in chapter 9.

Now, we want to know the conformation of adsorbed PEI with iron salts or iron chelates in the adsorption solution. With UV-vis absorption measurements the formation of iron EDTA chelates is confirmed. The PEI conformation is investigated with force-distance measurements, using the colloidal probe technique. Information on the grafting density and the thickness of the pseudo-brush is gained by changing the salt concentration in the measuring solution. To get some insight into the dynamics of the adsorbed PEI layer, swelling/shrinking cycles in different solutions are performed.

### 7.2 Results

For surface functionalization, three different solutions are used (i) salt-free water (pH = 9.3), (ii) solutions containing iron ions (2 mM FeSO$_4$, pH = 4.67) and (ii)
solution with iron chelates (4 mM FeSO$_4$ and 5 mM EDTA, pH = 3) at 21°C. Always, 2 mM PEI with respect to the monomer concentration is added.

**Figure 7.1:** Photograph of different solutions, from left to right: FeSO$_4$, before and after addition of PEI, FeSO$_4$ and EDTA after and before addition of PEI.

![Photograph of different solutions](image)

**Figure 7.2:** Extinction spectra of different solutions: PEI (black), FeSO$_4$ (red), PEI and FeSO$_4$ (orange), FeSO$_4$ and EDTA (pink) and PEI, FeSO$_4$ and EDTA (green). The respective concentrations are given in the legend. Note that all concentrations contain besides Fe$^{2+}$ also other components which are diluted compared to the adsorption solutions used for surface modification.

In Fig. 7.2, the respective UV-vis absorption spectra are shown. Clean water containing PEI is transparent in the visible region (cf. Fig. 7.1), at very low wavelengths (< 230 nm) the extinction increases. The solution containing iron ions is transparent, the addition of PEI turns it orange indicating the formation of PEI/iron complexes. For UV-vis measurements, the solution is diluted by a factor of one hundred, in order to quantify the increase of the extinction at wavelengths below 350 nm. FeSO$_4$/EDTA solution is light yellow (cf. Fig. 7.1), the addition of PEI turns it dark yellow, the extinction spectrum (of the diluted solution) shows a broad
peak at 260 nm which is attributed to iron chelates. On addition or removal of PEI
the position, the shape, and the intensity of the absorption peak remain the same.
Therefore, the iron chelates are stable upon addition of PEI and the slight change
in color is attributed to more diffuse scattering.

The surface forces between surfaces functionalized by a PEI layer adsorbed from a
salt-free solution are shown in Fig. 7.3(a). In agreement with previous experiments,
a flat adsorption layer is found [Pericet-Camara et al., 2006; Berg et al., 2013]. The
surface forces are repulsive, they are described by the DLVO theory for flat charged
surfaces [Israelachvili, 2011]. For monovalent salts of concentration $I$, at surface
separations $D$ larger than the Debye length $\kappa^{-1} = 0.304 \text{ nm} / I_{\text{NaCl}}^{0.5}$ and for surface
potentials $\psi_0 < 25 \text{ mV}$ the electrostatic repulsion is described by

$$F_{el}(D) = 0.0482 \sqrt{I_{\text{NaCl}}} \tanh^2 \left( \frac{\psi_0(\text{mV})}{103} \right) e^{-\kappa D (Jm^{-2})}$$

where $F_{el}$ denotes the electrostatic force, $\psi_0$ the surface potential at infinite surface
separation, and $I_{\text{NaCl}}$ the concentration of monovalent ions in the measuring solution
[Israelachvili, 2011]. The monoexponential decay with the surface separation $D$
described by Eq. 7.1 is observed in the force curves. Upon increase of $I_{\text{NaCl}}$ the
surface forces get more short-ranged. According to DLVO theory, the decay length
$\kappa^{-1}$ is not determined by surface properties, but only by the NaCl concentration,
$\kappa^{-1} = 0.304 \text{ nm} / I_{\text{NaCl}}^{0.5}$ (provided $I_{\text{NaCl}}$ is given in M). Fig. 7.4 shows that the
experimentally found decay lengths agree with the calculated Debye lengths.

If PEI is adsorbed from the second solution containing iron ions (2 mM PEI and 2
mM FeSO$_4$), the surface forces are subtly different (cf. Fig. 7.3(b)). Again repulsive
surface forces are found; again the range of the forces decreases upon increase of
the NaCl concentration in the measuring solution. Quantitatively, the range
of the repulsive forces is similar. Furthermore, on first sight one could describe the
repulsive forces with a mono-exponentially decaying function. However, there are
some problems concerning the dependence of the amplitude of the repulsive force
and the decay length on the NaCl concentration in the measuring solution. DLVO
theory predicts a decrease in the amplitude of the repulsive force upon increase of
the NaCl concentration. The decrease is caused by a decrease of the surface
potential (provided the surface charge is constant). Flatly adsorbed PEI does show
this behaviour [Pericet-Camara et al., 2006; Berg et al., 2013] as is demonstrated
in Fig. 7.3(a). However, for PEI adsorbed from a solution with 2 mM FeSO$_4$, the
amplitude of the repulsive forces is almost independent of the NaCl concentration.
Furthermore, the decay length $\lambda^{-1}$ decreases with increase of $I_{\text{NaCl}}$, but weaker than
7.2 Results

Figure 7.3: Force profiles acting between two surfaces covered with physisorbed PEI from adsorption solutions as indicated: (a) 2 mM PEI (with respect to the monomer concentration); (b) 2 mM PEI and 2 mM FeSO$_4$, (c) 2 mM PEI, 4 mM FeSO$_4$ and 5 mM EDTA. Varied is the NaCl concentration in the measuring solution: The NaCl concentration is indicated by arrows and given in mM, if not indicated otherwise. Fits to the DLVO and symmetric AdG theory (cf. Eq. 7.1) are symbolized by black straight and dashed lines, respectively. Each force curve shown is obtained by averaging over 100-150 approach curves.

predicted by DLVO theory (cf. Fig. 7.4). Therefore, we assumed that these are steric forces which are analysed by the theory of Alexander and de Gennes [Alexander, 1977; de Gennes, 1980, 1987] (called AdG theory below), since it was found to describe the interaction of grafted polyelectrolytes and pseudo-brushes prepared by adsorption of polyelectrolytes well [Liberelle and Giasson, 2008; Block and Helm, 2007; Balastre et al., 2002; Block and Helm, 2009, 2008, 2011]. De Gennes extended the theory of Alexander to describe the steric force acting between two end-grafted neutral polymer-brushes and calculated an interaction energy per unit area of two brushes (with thickness $L$ and grafting density $\Gamma = s^2$) to be
Chapter 7  PEI Layers Physisorbed in the Presence of Iron Ions and Iron Chelate

\[
\frac{F_{\text{AdG,sym}}(D)}{2\pi R} = \frac{8k_BT L}{35s^3} \left[ 7 \left( \frac{2L}{D} \right)^{5/4} + 5 \left( \frac{D}{2L} \right)^{7/4} - 12 \right] (Jm^{-2}) \text{ for } D < 2L \quad (7.2)
\]

The AdG force profiles are nonlinear functions which can be approximated well at intermediate surface separations \((0.2 < D/L < 0.9)\) by an exponential function with a decay length given by \(\lambda^{-1} = L/\pi\), which depends only on the brush thickness \(L\) [Liberelle and Giasson, 2008; Israelachvili, 2011; Balastre et al., 2002; Drechsler et al., 2010]. From least square fits of the force profiles to the AdG theory, \(L\) and \(s\) were determined (cf. Tab. 7.1, Tab. 7.2). Fig. 7.5(a) shows that the theoretically predicted scaling of polyelectrolyte brushes, \(L \propto (I_{NaCl}s^2)^{-\alpha}\) can be applied successfully to PEI chains adsorbed from 2 mM FeSO\(_4\). Within error, \(\alpha = 0.3\) (Fig. 7.5(a)) is close to theoretical predictions for the salted brush phase [Zhulina et al., 1995]. But this may very well be a coincidence; it is also possible that the dependence of \(L\) on \(I_{NaCl}\) and \(s\) deviates from theoretical predictions, since the theory was derived for linear polymer chains. Here branched polyelectrolyte chains were investigated.

Figure 7.4: Decay length \(\lambda^{-1}\) versus the NaCl concentration in the measuring solution as obtained by surface force measurements (shown in Fig. 7.3). Varied was the composition of the adsorption solution: gray dots symbolize salt-free water (2 mM PEI), red symbols solutions with iron ions (2mM PEI and 2 mM FeSO\(_4\)) and blue symbols solutions with iron chelates (2 mM PEI, 4 mM FeSO\(_4\), 5 mM EDTA). The black line is the theoretical Debye length according to DLVO theory. The green line is a guide to the eye. For the PEI layers physisorbed from solutions containing iron, always two different samples have been investigated (indicated by different red or blue symbols, respectively).

The amplitude of the force curves shown in Fig. 7.3(b) does not change very much upon increase in NaCl concentration. Thus, the average grafting density as determined from the amplitude of the force profiles is not constant as is the case for
chemically anchored polyelectrolyte brushes. Upon increase of the ion concentration, the average distance \( s \) between two PEI tails protruding into solution decreases monotonically, as shown in Fig. 7.5(b). The empirically determined correlation between the brush length \( L \) and the separation \( s \) between two anchored polymer chains is about linear. When \( L \) increases from 20 to 181 nm, then \( s \) increases from 28 to 74 nm. The increase of \( s \) is substantial, about a factor of two. An apparent increase of \( s \) was also observed for adsorbed linear polyelectrolytes (PSS, polylysine, poly(allyamine)hydrochloride) [Block and Helm, 2007], but it was always less than a factor of 1.5.

<table>
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<th>( I_{NaCl} ) [M]</th>
<th>( \lambda^{-1} ) [nm]</th>
<th>( L ) [nm]</th>
<th>( s ) [nm]</th>
<th>( \delta ) [nm]</th>
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Table 7.1: The parameters derived from least square fits of the force profiles shown in Fig. 7.3(b) to the AdG theory. PEI was adsorbed from a solution containing 2 mM PEI and 2 mM FeSO₄.

In the next step, a PEI layer was adsorbed from the third solution containing iron chelates (2 mM PEI, 4 mM FeSO₄, 5 mM EDTA). We expected that PEI is adsorbed in a coiled conformation since metal chelates bind electrostatically to branched PEI [Juang and Chen, 1996]. The force profiles (cf. Fig. 7.3(c)) can be more easily recognized as steric forces than those of PEI adsorbed from a solution containing iron ions (cf. Fig. 7.3(b)). In pure water and at low NaCl concentrations, the forces are not mono-exponential, but show a steep increase at very large surface separations. This feature is predicted by the AdG theory (cf. Eq. 7.2) when the brushes come
first into contact. However, the repulsive forces at first contact are weak and can only be resolved when the steric forces have a large amplitude, i.e., when the brushes are densely grafted. Additionally, as expected for polyelectrolyte brushes, swelling and shrinking upon change of the NaCl concentration in the measuring solution can be observed.

**Figure 7.5:** (a) Brush thickness \( L \) as a function of the product of \( (s^2) \) and ion concentration in the measuring solution. The straight lines are power law fits, the respective exponents are indicated. The brushes swell and shrink strongly by an order of magnitude. (b) Average distance between pseudotails \( s \), as a function of brush thickness \( L \). The lines are guides to the eye (same symbols as in Fig. 7.4).

Analysing the force curves gives quantitative values for the brush length \( L \) and the grafting density \( s^{-2} \) (cf. Fig. 7.5(a)). We find they are slightly smaller for decay length as for surfaces with PEI adsorbed from the solution containing iron ions only (2 mM PEI, 2 mM FeSO\(_4\); cf. Fig. 7.5). Also, the scaling of the brush length on \( s^2I_{\text{NaCl}} \) is the same within error (cf. Fig. 7.5(a)). At different NaCl concentration in the measuring solution, the grafting density is the same within resolution. Nevertheless, \( s \) depends strongly on \( I_{\text{NaCl}} \). When the brush length increases from 20 to 200 nm, \( s \) increases from 28 to 58 nm. This is a factor of two.

One conclusion is obvious: the PEI layer was adsorbed from a solution with iron salts, then the PEI layer was washed in clean water, and force measurements started. Washing removes the stabilizing iron ions or iron chelates. The brush shrinks and swells (cf. Fig. 7.6).
Table 7.2: The parameters derived from least square fits of the force profiles shown in Fig. 7.3(c) to the AdG theory. PEI was adsorbed from a solution containing 2 mM PEI, 4 mM FeSO$_4$ and 5 mM EDTA.

These are rather surprising results: we adsorbed branched PEI chains which are stabilized in a coiled conformation in solution. The coiled conformation was caused either by cooperative bonds between PEI and iron ions (2$^{nd}$ solution: 2 mM PEI, 2 mM FeSO$_4$) or by electrostatic bonds between PEI and iron chelates (3$^{rd}$ solution: 2 mM PEI, 4 mM FeSO$_4$, 5 mM EDTA). The chains adsorb in a coiled conformation and form electrostatic bonds between positively charged PEI monomers and negative charges on the silica surface. The grafting density for PEI adsorbed from a solution with iron chelates appears somewhat larger at low $I_{NaCl}$.

Unusual are the large changes in anchor density $s^{-2}$. The average distance $s$ between two chains decreases upon increase of the NaCl concentration. Such an effect can occur if some additional monomers adsorb to the substrate. This is very unlikely: upon increase of $I_{NaCl}$, the electrostatic shielding increases, and electrostatic bonds weaken. More probable is that conformation changes of the branched PEI lead to an apparent decrease of $s$ (cf. Fig. 7.6(b)). To explore segment desorption/adsorption, a few swelling/shrinking cycles were performed.

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<th>$I_{NaCl}$ [M]</th>
<th>$\lambda^{-1}$ [nm]</th>
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<td>28.8 ± 1.9</td>
<td>1.42 ± 0.1</td>
<td>S3</td>
</tr>
<tr>
<td></td>
<td>6.1</td>
<td>19 ± 0.8</td>
<td>30 ± 1.5</td>
<td>1.7 ± 0.1</td>
<td>S4</td>
</tr>
<tr>
<td>1</td>
<td>3.5</td>
<td>11 ± 2.6</td>
<td>38.4 ± 9.6</td>
<td>0.6 ± 0.2</td>
<td>S3</td>
</tr>
<tr>
<td></td>
<td>6.1</td>
<td>19.1 ± 2.5</td>
<td>34.3 ± 4</td>
<td>1.3 ± 0.1</td>
<td>S4</td>
</tr>
</tbody>
</table>
Figure 7.6: Force profiles acting between two surfaces covered with PEI layers adsorbed from a solution with iron chelates (2 mM PEI, 4 mM FeSO$_4$, 5mM EDTA). The solution was changed in the sequence indicated in the table on the right. Force curves in salt-free water were recorded after preparation (1, red), after shrinking in 1 mM and 1 M NaCl (3, brown), and subsequent swelling in 10 mM NaCl and salt-free water (5, black), followed by shrinking due to the salts of the adsorption solution (4 mM Fe$^{2+}$ and 5 mM EDTA), (6, blue) and again swelling in salt-free water (7, green). The average distance $s$ and the brush length $L$ given in the table on the right were determined by least square fits of the force profiles to AdG theory (cf. Eq. 7.2).

Branched PEI chains were adsorbed from a solution with iron chelates (cf. Fig. 7.6). PEI was first washed in clean water, then NaCl concentration was increased gradually (10 mM NaCl; 1 M NaCl), and subsequently decreased gradually (10 mM NaCl, salt-free H$_2$O). For the next shrinking/swelling cycle, the pseudo-brush was exposed to the ions of adsorption solution (4 mM FeSO$_4$, 5 mM EDTA) and then again to salt-free water. As expected, the first force curve in clean water is very similar to the one shown in Fig. 7.3(c): a thick brush ($L = 200$ nm). After shrinking in 1 M NaCl, upon the next immersion in clean water the brush length was increased ($L = 250$ nm), while $s$ remained unchanged compared to the previous experiment. However, after shrinking in the iron chelate solution, the brush swells again in pure water, but only up to 69% of the value obtained after preparation ($L = 138$ nm, 55% of the brush length obtained in the previous experiment). Furthermore, this force curve shows a small amplitude, suggesting a large separation between anchoring points. We conclude that almost collapsed PEI molecules in an iron chelate solution formed additional electrostatic bonds with the substrate. The force profiles of the shrunken PEI pseudo-brushes are very similar: in 1 M NaCl the brush length is 11.4 nm, in the iron chelate solution 10 nm. However, the effects of the different solutions on the adsorbed PEI are opposite: while immersion in 1 M NaCl promotes segment detachment of individual PEI segments from the surface,
immersion in iron chelate solution promotes segment attachment to the surface.

Some questions remain open: when lipid monolayers were investigated, it was found that PEI layers were thicker when formed from an iron chelate solution instead of a solution with ion irons [Gröning et al., 2016]. The same trend is observed if PEI was adsorbed onto Si wafers (cf. Fig. 7.5). The meaning of this result is not clear since the formulas were derived for linear polyelectrolytes, yet we work with branched polyelectrolytes. Therefore, we wanted to find out if the surface functionalization is different, if PEI layers were adsorbed from different solutions. We adsorbed AuNPs onto PEI functionalized surfaces; the difference of the PEI layer at the surface was caused by the composition of the solution from which PEI was adsorbed. Due to the low concentration of AuNP in the solution (2.4 nM), the time dependence of AuNP number density is determined by the diffusion of the AuNP to the surface. Assuming that each AuNP which touches the surface, adsorbs irreversibly; the number density $\Gamma$ of AuNPs (surface coverage) increases with time according to (cf. Sec. 4.2)

$$\Gamma = 2c_{AuNP} \sqrt{D \cdot t / \pi}$$  \hspace{1cm} (7.3)

where $c_{AuNP}$ is the concentration of gold nanoparticles in solution, $D$ their diffusion constant in solution and $t$ the adsorption time of the AuNPs.

![Figure 7.7: Extinction spectra of gold nanoparticles adsorbed onto PEI-functionalized surfaces for different immersion times. The PEI layer was prepared by physisorption from a solution containing 2 mM FeSO$_4$. The immersion times are 45, 90, 110, 195, 231, 300 and 1440 min (bottom to top, left side).](image-url)
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Figure 7.8: Extinction spectra of gold nanoparticles adsorbed onto PEI-functionalized surfaces for different immersion times. The PEI layer was prepared by physisorption from a solution containing 4 mM FeSO$_4$ and 5 mM EDTA. The immersion times are 45, 90, 110, 195, 231, 300 and 1440 min (bottom to top, left side). The immersion times are 30, 45, 90, 150, 167, 301, 1140 and 1440 min (bottom to top, left side).

The surface coverage increases until maximum coverage is reached [Schmitt et al., 1999]. Fig. 9.9 (chapter 9) demonstrates with AFM images of the surfaces the increasing number density with adsorption time. The maximum number density is obtained after 240-360 min. Absorption spectra of PEI functionalized surfaces confirm this finding, yet differences for the different surface functionalizations are found, depending on the composition of the deposition solution of PEI (cf. Fig. 7.7 and Fig. 7.8). If the surfaces are functionalized with PEI adsorbed from pure water or a solution containing iron ions (2 mM FeSO$_4$), then a typical absorption peak of AuNPs with a maximum at 530 $\pm$ 1 nm is observed. With increasing adsorption times, the intensity of the peak increases. After three to four hours the maximum peak intensity is reached.

However, if PEI was adsorbed from an iron chelate solution (4 mM FeSO$_4$, 5 mM EDTA), then after 45 min immersion time of the AuNPs a second peak at ca. 600 nm appears. Upon increase of the immersion time, the peak maxima differ in intensity, but not in position. This double peak can be found if two particles aggregate. In this case, in the quasi-static approximation, two plasmons can be excited, one perpendicular to the pair axis whose absorption is basically unchanged) and one parallel to the pair axis whose absorption peak is red shifted due to a more extended plasmon [Schmitt et al., 1999; Ghosh and Pal, 2007]. Presumably, PEI chains dangling into the solution may adhere to two gold colloids simultaneously, causing a bridging-atraction. From the peak intensity, the surface coverage is calculated according to [Schmitt et al., 1999]:

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7.2 Results

\[ \Gamma = \frac{\gamma_{\text{monolayer}}}{\gamma_{\text{bulk}}} \cdot c_{\text{AuNP}} \cdot d_{\text{monolayer}} \]  \hspace{1cm} (7.4)

with \( \gamma_{\text{monolayer}} \) and \( \gamma_{\text{bulk}} \) as the extinction maxima of the monolayer and the bulk solution, respectively, and \( d_{\text{monolayer}} \) the thickness of the gold monolayer which is assumed to be identical with the diameter of the AuNPs (16 nm). Eq. 7.4 has about 15% error, since the intensity of an absorption maximum depends on the dielectric constant of the immediate environment of the AuNPs. We used the intensity of the absorption peak of AuNPs on PEI functionalized surfaces to determine the time dependence of the number density of AuNPs. Eq. 7.3 predicts that it increases with the square root of adsorption time. This is indeed observed for all PEI functionalized surfaces (cf. Fig. 9.10, chapter 9). From the time dependent increase of the number density the diffusion constant is determined, \((2.4 \pm 0.9) \times 10^{-11} \text{m}^2/\text{s}\). This value is in agreement with previous findings, and also with the Stokes-Einstein equation [Schmitt et al., 1999; Ghosh and Pal, 2007; Berg et al., 2013].

While we get the same time dependence of the AuNP number density for all PEI functionalized surfaces, the UV-vis spectra of the surfaces after 24 hours differ drastically, one peak or two peaks. This indicates isolated or aggregated AuNPs, respectively. Therefore, it is not clear if the maximum number density is the same. To address this questions, AFM images of the three PEI functionalized surfaces with maximum AuNPs coverage were compared (cf. Fig. 7.9).

![AFM images](image)

**Figure 7.9:** AFM tapping mode height images (1 \( \times \) 1 \( \mu m^2 \)) of AuNPs adsorbed onto PEI functionalized surfaces which were physisorbed from different solutions: (a) 2 mM PEI, (b) 2 mM PEI + 2 mM FeSO\(_4\) and (c) 2 mM PEI+ 4 mM FeSO\(_4\) + 5 mM EDTA. The adsorption time from AuNPs solution was 24 hours. All measurements are performed in air. Scale bars: 200 nm.

Qualitatively, one recognizes that on flatly adsorbed PEI the surface coverage is lower than on PEI adsorbed from a solution containing iron ions (2 mM FeSO\(_4\)). However, when PEI is adsorbed from iron chelate solution, the AuNPs aggregate. Dimers, trimers and oligomers can be distinguished. Most aggregates are tilted
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with respect to the surface plane. The AuNP number density can be determined for the isolated AuNP to be 910 and 1220 AuNP/µm², for PEI adsorbed from pure water and a solution containing iron ions, respectively. We also counted the aggregated AuNPs on PEI adsorbed from the iron chelate solution and obtained 730 AuNP/µm², but this number is too low since we cannot distinguish oligomers from a single nanoparticle.

To determine the AuNP number density unambiguously, X-ray reflectivity measurements were performed (cf. Fig. 7.10). Independent of the way the surfaces were PEI functionalized, the X-ray reflectivity curves always show three interference maxima. Yet, there are subtle differences. If PEI was adsorbed from pure water or from a solution containing iron ions (2 mM FeSO₄), the position of the maxima and minima is identical, indicating an identical thickness of the AuNP layer. However, the maxima have a larger amplitude if PEI was adsorbed from a solution containing iron chelate (4 mM FeSO₄, 5 mM EDTA), the maxima and minima of the X-ray reflectivity curves shift to lower $Q_z$-values, while the intensity remains constant.

Quantitative analysis of the X-ray reflectivity data yields electron density profiles (cf. inset in Fig. 7.10). The detailed model of the electron density profile and its parameterization is described in the Sec. 9.4. We assume that PEI partly forms a spacer layer beneath the AuNPs, and partly penetrates between the AuNPs. The AuNPs are assumed to be spherical (radius 8 nm), yet with a size distribution (variance 0.4 nm). The exact parameters of the electron density profiles are determined by least square fits to the X-ray reflectivity curves. The surface coverage of AuNPs on PEI adsorbed from pure water is significantly lower (743 AuNP/µm²) than on PEI adsorbed from a solution containing iron ions or ion chelates (942 and 1040 AuNP/µm², respectively). For isolated AuNPs, the results from AFM and X-ray reflectivity agree quantitatively. Additionally, the thickness of the PEI spacer layer depends on the composition of the PEI adsorption solution: it is very thin (0.2 nm) if PEI was adsorbed from pure water or a solution containing iron ions. If PEI was adsorbed from a solution containing iron chelates, it is thicker than a flatly adsorbed PEI monolayer (0.6 nm). Additionally, PEI penetrates between the AuNP. Most PEI between the AuNPs is found if PEI was adsorbed from a solution containing iron chelates, with the least PEI if PEI was adsorbed from salt-free water. PEI surface coverage is determined by vertically integrating along the electron density profile, and calculating segments per nm². If PEI surface coverage is compared we obtain for the force curves a dependence on the composition of the adsorption solution, iron chelate > iron ions > pure water.
7.2 Results

Figure 7.10: X-ray reflectivity measurements of AuNPs layers on PEI surfaces which were physisorbed from different solutions: 2 mM PEI (black), 2 mM PEI and 2 mM FeSO₄ (red), and 2mM PEI, 4 mM FeSO₄ and 5 mM EDTA (blue). Adsorption time of AuNPs was 24 hours. The measurements are points, the lines least square fits. Inset: electron density profile derived from the fits. For clarity, the reflectivity curves are shifted vertically.

Fig. 7.11: Normalized X-ray reflectivity measurements in air. PEI was adsorbed from salt-free water (cyan). PEI was adsorbed from 2 mM FeSO₄ solution and then rinsed with Millipore water (blue). PEI was immersed in 2 mM FeSO₄ solution (brown).

Fig.7.11 shows normalized X-ray reflectivity measurements in air. The samples were prepared differently: PEI was adsorbed from salt-free water (cyan), PEI was adsorbed from 2 mM FeSO₄ solution and then rinsed with Millipore water (blue) or PEI was immersed in 2 mM FeSO₄ solution (brown). PEI concentration was always
2 mM with respect to monomer concentration. The normalized reflectivity curves of the first two films are very similar: they have a minimum at almost the same position (0.172 Å\(^{-1}\) and 0.184 Å\(^{-1}\), respectively), and then a clear maximum at almost identical positions (0.289 Å\(^{-1}\) and 0.286 Å\(^{-1}\)). Qualitatively, the reflectivity curve of the third film (brown) is similar: it shows a minimum followed by a maximum. However, the positions of both extremes are shifted to smaller \(Q_z\)-values indicating an increased film thickness.

These measurements suggest the following conclusion: PEI adsorbed from a FeSO\(_4\) solution adsorbs together with the Fe\(^{2+}\) ions. The Fe\(^{2+}\) ions can be removed by rinsing the substrate in Millipore water. Then, only the PEI film remains.

### 7.3 Discussion

We used three different adsorption solutions to functionalize surfaces with branched PEI: pure water (pH = 9.3), solutions containing iron ions (2 mM FeSO\(_4\), pH = 4.67) and solutions containing iron chelates (4 mM FeSO\(_4\), 5 mM EDTA, pH = 3). Always, the PEI concentration was 2 mM with respect to the monomer concentration.

We investigated the PEI conformation with surface forces measurements using the colloidal probe technique. PEI adsorbed from pure water adsorbed flatly, as described previously [Szilágyi et al., 2014; Pericet-Camara et al., 2006; Berg et al., 2013]. If PEI was adsorbed from solutions containing iron ions or iron chelates, steric forces were observed. In both cases, PEI formed a pseudo-brush as described for linear polyelectrolytes adsorbed from solutions containing a high concentration of monovalent salts [Szilágyi et al., 2014; Block and Helm, 2008]. The thickness of the pseudo-brushes showed the same dependence on the concentration of NaCl in the measuring solution as is known for polyelectrolyte brushes in the salted brush phase [Ahrens et al., 1998]. Brush thickness (surface force measurements, Fig. 7.3) and x-ray reflectivity (cf. Fig. 7.3) measurements indicate larger surface coverage for PEI adsorbed from a solution containing iron than of PEI adsorbed from salt-free water. The brush thickness is largest if adsorbed from a solution containing iron ions, while the surface coverage appears to be larger when PEI adsorbed from a solution containing iron chelates.

PEI solutions show different pH values when existing with iron chelates (pH = 3), and iron ions (pH = 4.67) or in salt-free in water (pH = 9.3) at room temperature. The surface coverage was determined with X-ray reflectivity; it was largest for PEI adsorbed from iron chelate solution. Although pH of the PEI solution with iron chelates, and iron ions are lower than PEI salt-free in water, the surface coverages
of the PEI were higher in the first two cases. This is inconsistent with the observation from Varga [Varga et al., 2011], which shows the surface coverage of PEI (physisorbed from 10 mM) increases with increasing pH. In our observation, the influence of iron ions and iron chelates on the surface coverage of PEI physisorbed film is stronger than pH effect. Different from PEI adsorbed from salt-free solution, which shows flat conformation, surface force measurements with colloidal probe microscopy show for PEI adsorbed from iron chelates or iron ions layers almost identical long ranged steric forces. The brush thickness scales like polyelectrolyte brushes as calculated from the force-distance profiles as a function of the ionic strength in the measuring solution. The brush thickness measured with CPT is much larger than the brush thickness measured using other optical techniques, such as ellipsometer, that the AFM measures the range of forces through charges which have a more extended effect than the absolute thickness of the brush which is measured by ellipsometer and depends on the refractive index of the materials. Successive swelling and shrinking experiments show that fractions of the PEI chain desorb and re-adsorb, provided PEI was adsorbed from a solution containing iron chelates. The observation that higher surface coverage of the PEI leads to steric or electro-steric interaction forces was also found by Notley [Notley and Leong, 2010]. It is interesting to observe that PEI does not adsorb from a solution with pH = 3 and monovalent ions (Fig. 9.11, Appendix). However, a large PEI surface coverage can be obtained if the solution also contains iron chelates.

Note that the intermolecular forces causing the coiled conformation of PEI in the adsorption solution and on the substrate are very different: if adsorbed from high concentrations of monovalent salt, one obtains a coiled conformation because of decreased electrostatics. The persistence length is shortened, and the intersegment interaction is less repulsive. These effects can be described with mean-field theory [Flory, 1969; Netz and Andelman, 2003]. However, Fe$^{2+}$ ions interact with PEI via cooperative bonds, and iron chelates via electrostatic bonds. These are bi-directional interactions which cannot be described by mean-field theories. Nevertheless, the bonds are weak. Both iron ions and iron chelates can be removed from adsorbed PEI by washing the polymer layer with salt-free water. It is new and very interesting that adsorption and desorption events could be induced in a PEI layer adsorbed from iron chelate solution was sequentially exposed to (i) salt-free water, (ii) 1 M NaCl solution, (iii) salt-free water, (iv) adsorption solution and (v) salt-free water. The brush thickness in salt-free water increased from (i) to (iii), and decreased from (iii) to (v). Additionally, from (iii) to (v), the apparent grafting density decreased. Thus, exposure to 1 M NaCl led to segment desorption, exposure to the deposition solution (4 mM FeSO$_4$, 5 mM EDTA) to
segment adsorption. Such an effect was not observed if the polyelectrolytes were adsorbed from solutions containing high concentrations of monovalent salt [Szilágyi et al., 2014; Block and Helm, 2008].

We investigated the molecular mass dependence of polyelectrolyte pseudo-brushes adsorbed from 1 M NaCl. It is simple: the brush thickness is proportional to the molecular mass [Block and Helm, 2009]; it could amount to 2/3 of the contour length. This finding suggested that the polyelectrolyte adsorbed as a train and tail (no loop), and the train was the smaller fraction. Here, it is different. Due to the directional bonds between segments and divalent ions or chelates, respectively, more loops are expected. According to the work of Hermann E. Gaub [Friedsam et al., 2004; Hugel et al., 2001] the desorption energy of a polymer chain is proportional to the energy of the monomer substrate ionic bond multiplied by the number of monomers. For a long train the desorption energy is higher than for a short train. In case of polyelectrolytes adsorbed from 1 M NaCl, there is one long train and no desorption. If PEI adsorb coils, which are stabilized by directional forces caused either by electrostatic binding with EDTA or cooperative bonds with Fe$^{2+}$ then, there are more small pearls within the polymer coil, and thus more short trains on the substrate. The short trains desorb when exposed to 1 M NaCl solution, and re-adsorb when exposed to the deposition solution. Investigation of the dependence of segment/substrate binding on $I_{NaCl}$ shows that the electrostatic contribution to substrate/segment binding decreases with $I_{NaCl}$ [Friedsam et al., 2004; Hugel et al., 2001].

Therefore, the shielding of electrostatic forces is strongest, and desorption of short trains is most likely. Exposure of the PEI layer to the deposition solution not only shrinks the layer, but also crumples it due to the formation of directional bonds between iron chelates and monomers. This may be the mechanism by which short fractions of the chains approach the substrate and adsorb.

These thoughts suggest that the adsorption of polyelectrolyte coils with specific bonds leads to polymer layers which are more likely to rearrange on a molecular level. Additionally, short branches may easily desorb or adsorb.

When we started the project, we aimed to design polymer layers with specific properties, based on the understanding of the hierarchy of intermolecular forces. Now we find that the surface forces of PEI layers adsorbed from solutions containing iron chelates or iron ions show very similar force profiles. The adsorbed PEI layers can be described as polyelectrolyte pseudo-brushes. The maximum surface coverage of AuNPs adsorbed on these layers is also the same within error. In the AuNP solution the Debye-length is about 4 nm [Eck, 2000], this corresponds to a brush length of
about 20 nm (cf. Fig. 7.9, Tab. 9.6, Tab. 7.2). The brush length exceeds the diameter of the AuNPs (ca. 16 nm). Apparently, brushes with a length exceeding the AuNP provide a more effective surface functionalization than just charge reversal, allowing a larger maximum number density of AuNPs to be achieved.

There is an open question: on one polymer layer the AuNPs aggregate, and on one they don’t. The reasons for the different surface properties are subtle; X-ray reflectivity measurements indicate that the PEI coverage is higher when adsorbed from an iron chelate solution, a finding which is consistent with investigations of monolayers at the air/water interface and the observed dependence of PEI surface coverage on the composition of the adsorption solution [Gröning et al., 2016].

The different surface coverage has two implications: (i) one implication concerns the interpretation of surface forces. The steric forces caused by the pseudo-brushes are not a measure of the surface coverage. In the AdG theory, the parameter $s$ describes the average distance between anchored tails, and determines the amplitude of the steric forces. But in our measurements, $s$ is almost the same for PEI layers adsorbed from solution containing iron ions or iron chelate irons. However, for grafted polymer brushes a larger surface coverage is equivalent to a smaller $s$. A possible reason for this inconsistency is the fact that PEI is a branched polymer, and chains are not only grafted to a substrate, but to a polymer chain. In a first approximation $s$ is a measure of the grafting density of the pseudo-brushes at a distance away from the substrate (this distance is not known). There is no direct relationship between $s$ and the surface coverage. (ii) The other implication concerns the ability of the AuNPs to aggregate. The pseudo-brushes are very similar, both in brush length, and average distance between tails, however the adsorbed trains may differ. Therefore, the electrostatics within the brush and on the outer brush surface is also identical. However, an adsorbed PEI layer can rearrange on a molecular level. Some fractions of the molecule can desorb or adsorb (cf. Fig. 7.9). Apparently, if the surface coverage is larger, PEI can more easily rearrange to provide bridging forces between AuNPs inducing aggregation. This interpretation is in agreement with X-ray reflectivity measurements (cf. Fig. 7.10) which show more PEI between the aggregated AuNPs.

### 7.4 Conclusion

We investigated new ways to functionalize a surface with an adsorbed polyelectrolyte layer, when the surface and the polyelectrolyte bear opposite charges. We used a branched polyelectrolyte, and two different adsorption solutions with divalent iron.
ions with the same charge as the polyelectrolyte or oppositely charged iron chelates. Cooperative bonds between segments and the divalent ions are directional, as are the electrostatic bonds between different segments and a chelate within a polymer coil. From both solutions, the polyelectrolytes adsorb as coils. The divalent ions and the iron chelates can be removed from the adsorbed polyelectrolyte layer by washing in salt-free water. Then, the adsorbed polyelectrolyte layer behaves as a polyelectrolyte brush, it swells and shrinks depending on the concentration of the surrounding salt solution. The thickness changes of the pseudo-brush can be described by the scaling laws of polyelectrolyte brushes.

Nevertheless, the grafting density of the pseudo-brushes deduced from the surface forces is not correlated to the surface coverage. Other methods than surface forces are necessary to determine the surface coverage of a polyelectrolyte pseudo-brush. We used X-ray reflectivity.

The maximum number density of AuNPs adsorbed onto PEI pseudo-brushes was identical and larger than of AuNPs layers adsorbed onto flatly adsorbed PEI. On the PEI layer with the larger surface coverage, the AuNPs aggregate; on the PEI layer with the lower surface coverage they do not aggregate. For AuNP aggregates, polyelectrolyte chains have to provide attractive bridging forces between the AuNPs. This happens only if the surface coverage is sufficiently large, and the PEI chains can rearrange on a molecular level. Swelling/shrinking cycles of a PEI layer prepared from an iron chelate solution showed an increase and decrease of the apparent brush length in clean water indicating adsorption/desorption events. Right now, the respective role of directional forces (cooperative bonds, or weak electrostatic bonds with oppositely charged chelates) and the branching of PEI in the occurrence of molecular needs further investigations.
8 Summary

Polyelectrolytes remain among the least understood materials in soft matter, despite their widespread presence and use. One common use is surface functionalization when polyelectrolytes adsorb with many weak electrostatic bonds. Thus, they form durable coatings. They are employed in a multitude of applications; an example is water purification [Rivas et al., 2003]. The surface coverage is often known [Szilágyi et al., 2014; Butt and Kappl, 2010], however there is no clear relationship between surface coverage and conformation. Therefore, surface functionalization is empirically optimized. The adsorption conditions are varied, and the physical properties of the polymer film are determined. Furthermore, polyelectrolyte brushes attracted some attention in recent years because the increased ion concentration in the brush compared to the solution facilitates or hinders reactions [Lu and Ballauff, 2016; Wittmann et al., 2003], also it affects the adsorption of oppositely or equally charged nano-objects [Ballauff, 2007]. However, the conformation and the surface charge of polyelectrolytes on surfaces is known only in a few cases.

In this work, my first aim was to study a monolayer of branched poly(ethylenimine) (PEI) adsorbed onto oppositely charged surfaces with iron chelates or iron ions in the absorption solution. The conformation of adsorbed PEI is explored in the dependence of the composition of the adsorption solution by measuring the surface forces using AFM with colloidal probe technique (CPT) at different ionic strengths in surrounding aqueous solution. The surface coverage of these layers is also investigated using X-ray reflectivity.

The branched PEI contains a high number of amino groups. They have the ability to donate electrons and chelate metal ions. Through a coordination interaction bond [Maketon et al., 2008], a few amino groups of PEI can interact with one metal ion [Jarvis and Wagener, 1995; Kobayashi et al., 1987]. PEI solutions show different pH values with iron chelates (pH = 3), iron ions (pH = 4.67) or pure water (pH = 9.3) at room temperature. Low surface coverage of PEI at pH = 3 adjusted by monovalent ions was observed [Mészáros et al., 2004; Varga et al., 2011]. However, PEI with iron ions or iron chelates adsorp and washing with pure water shifts the pH, leading to an adsorbed PEI layer with high coverage. In our
observation, the influence of iron ions and iron chelates on the surface coverage of physisorbed PEI film is stronger than the pH effect. PEI adsorbed from salt-free solution shows flat conformation. Surface force measurements with colloidal probe microscopy show that PEI adsorbed from solution containing iron chelates or iron ions layers, which cause almost identical long-ranged steric forces. The thickness of the pseudo-brush is determined as a function of the ionic strength (NaCl) in the measuring solution. It scales as a polyelectrolyte brush. The thickness of the pseudo-brush measured using atomic force microscopy (AFM) through CPT is much larger than the brush thickness measured using other optical techniques such as ellipsometer. The AFM measures the range of forces. The absolute thickness of the brush measured by ellipsometer depends on the refractive index gradient of the brush. Successive swelling and shrinking experiments show that fractions of the PEI chain desorb and re-adsorb, provided PEI was adsorbed from a solution containing iron chelates. PEI adsorbs from solutions with pH = 3 only if the solution contains ion chelates, resulting in a high surface coverage and a layer with pseudo-brushes.

The maximum number density of gold nanoparticles adsorbed onto the PEI pseudo-brushes was identical and larger than on flatly adsorbed PEI. On the PEI layer with the larger surface coverage prepared from a solution containing iron and EDTA, the nanoparticles aggregate; on the PEI layer with lower surface coverage they do not aggregate. A correlation between adsorption/desorption events and bridging forces between Au nanoparticles is discussed. Taken together, these results contribute to understanding the mechanisms determining surface coverage and conformation of adsorbed polyelectrolytes and demonstrate the possibility of controlling surface properties, which is highly desirable for potential future applications.

The second aim of the thesis is to investigate the top layer (PSS and PDADMA) of polyelectrolyte multilayer films, and how the structure of the physisorbed top layer can be controlled.

Polyelectrolyte multilayer films (PEMs) were prepared by sequential adsorption of oppositely charged polyelectrolytes on solid substrates. Polyelectrolyte multilayer films consist of polydiallyldimethylammonium (PDADMA) as polycation and the polystyrenesulfonate (PSS) as polyanion. The polycation PEI was used exclusively for a first functionalization layer of the substrate. All PEMs were adsorbed at 0.1 M NaCl with 1 mM monomer concentration at room temperature (about 20° C) and neutral pH. Because of the differing monomer length of PDADMA (0.54 nm) and PSS (0.25 nm), PSS has twice the linear charge density as PDADMA. I studied the top layer (PSS and PDADMA) conformation of polyelectrolyte multilayer films and how the structure of the physisorbed top layer is affected by increasing the
number of layer pairs and the addition of salt to the surrounding solution specially at the almost biological ion concentration (0.1 M NaCl). A better understanding of the surface forces ruling the adsorption of polyelectrolytes was achieved with help from AFM and its specific CPT as the high-resolution technique. It is possible in this way to gain more insight into the surface charge, the surface potential, and the conformation of the top layer of polyelectrolyte multilayer film.

An investigation of the surface forces of polyelectrolyte multilayer films with PSS as the top layer at a different number of layer pairs is presented. The ionic strength has been changed systematically and force-distance measurements at different salt concentration have been performed. PSS terminated films always show electrostatic forces at ionic strength < 0.1 M, which are due to a flat PSS conformation. As a representative example for the parabolic growth regime, a film consisting of N = 9 PDADMA/PSS layer pairs is investigated. The surface charge density is always negative at ionic strength < 0.1 M. The surface charge of the PSS top layer starts to turn from negative to positive at a number of PDADMA/PSS layer pairs N ≥ 14. These findings correlate well with different studies from [Ghostine et al., 2013; Arias et al., 2016; Nestler et al., 2013] for the PDADMA/PSS films. The PDADMA terminated surface contains many positive sites. The density of the positive sites grows with increase of the layer pairs. At layer pairs between 13 and 15, adsorbed PSS cannot compensate all the excess PDADMA charge. This leads to an accumulation of the positive extrinsic sites within the PSS terminated film beyond a specific number of layer pairs [Ghostine et al., 2013]. At an ionic strength around 0.1 M, an exponential decaying force was measured. This is an indication of unusual long-ranged hydration force (decay length ≈ 0.2-0.5 nm), also PSS terminated film shows zwitterionic or neutral surface. At ionic strength > 0.1 M, a non-electrostatic action occurs and the PSS terminated film reswells in solution. This effect has been observed also by [Biesalski et al., 2004; Mei and Ballauff, 2005]. I conclude that the surface charge of the PSS film is determined by a chemical equilibrium using the law of mass action and monomer conservation at the surface:

\[
\begin{align*}
[\text{Pol}^- \cdot \text{Pol}^+] + [\text{Pol}^+ \cdot \text{Cl}^-] + [\text{Pol}^- \cdot \text{Na}^+] + [\text{Pol}^+] + [\text{Pol}^-] &= \text{const.}
\end{align*}
\]

Pol\(^+\) and Pol\(^-\) denote PSS and PDADMA monomers, the brackets concentrations. When [Na\(^+\)] and [Cl\(^-\)] are decreased, fewer ions are bound on the surface and [Pol\(^+\)] and [Pol\(^-\)] increase. Depending on the composition of the surface, the film is positively or negatively charged. If [Na\(^+\)] and [Cl\(^-\)] are increased beyond 0.1 M, then [Pol\(^-\) Na\(^+\)] and [Pol\(^+\) Cl\(^-\)] increase and more ions bind to the chains. At the
same time, less ionic monomer-monomer bonds \( ([\text{Pol}^- \text{Pol}^+] ) \) bind the chains to the surface. Therefore, some chain fractions are no longer attached to the film but dangle into solution.

The surface forces of PDADMA terminated polyelectrolyte multilayer films consisting of a different number of layer pairs were also investigated. At films consisting of one and 5 layers, PDADMA shows a flat conformation and the electrostatic forces were measured. For \( N = 9, 14, 17, 19 \) and ionic strength \( \leq 0.1 \text{ M} \), long-range steric forces were measured. The force-distance profiles are well-explained by Alexander and de Gennes’ theory for neutral end-grafted polymers. PDADMA chains show a maximum brush length that is around 40-45% of the contour length. For ionic strength, \( I \approx 0.1 \text{ M} \), and \( N > 9 \), a flat, neutral or zwitterionic surface is found (decay length \( \lambda^{-1} \approx 0.3-0.9 \text{ nm} \)). For \( N = 9 \) and ionic strength \( > 0.1 \text{ M} \), a strong screening of electrostatic interaction and attractive forces are observed. For \( N > 9 \) and ionic strength \( > 0.1 \text{ M} \), the ion adsorption into the polyelectrolyte chains leads to an increase in the monomer size [Mei and Ballauff, 2005] and as a result, the brush thickness \( L \) increases and PDADMA brushes protrude again into the solution. PSS and PDADMA terminated surfaces show this ion adsorption into the chains (reswelling) but for PSS this effect starts earlier with the number of layer pairs \( (N = 9) \) compared to PDADMA.

These data show that by varying the number of layer pairs and the ionic strength, different surface forces can be obtained: Electrostatic forces (flat chains) both positive and negative, steric forces (pseudo-brush), hydration force (flat, neutral or zwitterionic surface), and effects not yet explained (reswelling brush) are observed.
Bibliography


Bibliography


9 Appendix

9.1 Forces-distance between silica surfaces

Purely repulsive or positive forces were measured between CP silica spheres and silica surface in aqueous solution with NaCl concentration between 0 and 1 M. Only the approach force profiles in logarithmic scale normalized to the CP radius R are introduced (Fig. 9.1 (left, dots)). A simple exponential decay fit (Eq. 9.1), the constant potential approximation, was done for the direct force measurements as shown in Fig. 9.1 (left, lines). The fitting parameters, surface potential $\psi_{0,\text{SiO}_2}$ and Debye length $\kappa^{-1}$ are given in Fig. 9.2 and Tab. 9.1. The repulsive forces between silica surfaces are well described with Debye-Hückel approximation as expected and measured before.

![Diagram](image)

**Figure 9.1:** (Left) The force-distance profiles (dots) measured between silica CP and silica surface at different ionic strength I (indicated arrows) and the corresponding linear fits according to the DLVO theory for the electrostatic forces of the electric double layer (solid lines) in the constant potential approximation case. (Right) The fitted decay length (circles) from the measured forces profiles (left). The Decay lengths are matched to the theoretical Debye length (dash lines) according to (Eq. 3.21).
\[
\frac{F_{DH}(D)}{2\pi R} = 64 \frac{k_B T}{\kappa} \tanh^2 \left( \frac{e\psi_0}{4k_B T} \right) e^{-\kappa D} = 0.0482 \sqrt{I_{NaCl}} \tanh^2 \left( \frac{\psi_0 \text{mV}}{103} \right) e^{-\kappa D}
\]
(9.1)

The fitted decay lengths \( \lambda^{-1} \) from the direct force measurements agreed well with the theoretical Debye length \( \kappa^{-1} \) which was calculated using Eq. 3.21. The decay length deviates from the theoretical Debye length at surface separation \( D \) smaller than theoretical Debye length due to the charge regulation [Pericet-Camara et al., 2004; Popa et al., 2010b]. Silica surface is negatively charged in water due to the dissociation of the silanol groups on the surface which leads to negative surface potential [Papirer, 2000]. To calculate the surface charge density \( \sigma_{0,\text{SiO}_2} \), Grahame’s equation (Eq. 9.2) is used. A small deviation from \( 2 \text{ mC/m}^2 = \left( \frac{e}{80 \text{ nm}^2} \right) \) is found. The surface charge density increases slightly with increased NaCl concentration as shown in Fig. 9.2 and Tab. 9.1.

\[
\sigma_0 = \sqrt{8k_B T \varepsilon_0 \varepsilon_{\infty} \sinh \left( \frac{e\psi_0}{2k_B T} \right)} = 0.117 \sqrt{I_{NaCl}} \sinh \left( \frac{\psi_0 \text{mV}}{51.5} \right)
\]
(9.2)

**Figure 9.2:** (Left) The surface potential of silica surface fitted using the force-distance profiles ((Fig. 9.1), left) and Eq. 9.1 of simple exponential of the Debye Hückel (DH) approximation which shows a dependence on the ionic strength \( I \). (Right) The surface charge density \( \sigma_{0,\text{SiO}_2} \) is calculated by applying Grahame’s equation (Eq. 9.2) to the fitted \( \psi_{0,\text{SiO}_2} \).

These fitting parameters for this system are compared with previous work by Serr [Serr, 2003] and Block [Block, 2010] in Tab. 9.1. Block used the same approach conditions for colloidal probe technique (CPT), but Serr did the experiments at pH = 6 for KCl, both of which found a good agreement.
Table 9.1: The electrostatic parameters obtained from the force-distance measurements ((Fig. 9.1), left) fitted according to (Eq. 9.1). The second column compares the theoretical Debye length with the measured decay length in the third column and the third one shows the measured surface potential of silica $\psi_{0, \text{SiO}_2}$. The last column shows the surface charge density $\sigma_{0, \text{SiO}_2}$ as obtained by applying Grahame’s equation, (Eq. 9.2), to $\psi_{0, \text{SiO}_2}$.

<table>
<thead>
<tr>
<th>$I_{\text{NaCl}}$ [mM]</th>
<th>$\kappa_{\text{theo.}}$ [nm]</th>
<th>$\lambda_{\text{meas.}}$ [nm]</th>
<th>$\psi_{0, \text{SiO}_2}$ [mV]</th>
<th>$\sigma_{0, \text{SiO}_2}$ [mC/m$^2$]</th>
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</tr>
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<tr>
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<tr>
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<tr>
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<td>-3(0.97)</td>
</tr>
<tr>
<td>50</td>
<td>1.36</td>
<td>1.5</td>
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<td>-4(1.4)</td>
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</tbody>
</table>

In CPT, the surface separation $D$ is calculated using the measured data, which may lead to an underestimation of the $D$ values. In contrast, the surface force apparatus (SFA) can be used as an interferometric technique to measure the absolute value of $D$. This underestimation of $D$ could also happen due to the surface roughness which produces a slight shift [Block, 2010]. As a dependence parameter of $D$ (plane of origin ($D = 0$), (Eq. 6.1)), the surface potential deviates from measured values with other techniques like SFA [Horn et al., 1989].

Table 9.2: Different literature data for surface potential $\psi_{0, \text{SiO}_2}$ compared to this work. Symmetric CPT measurements on silica surfaces (pH = 6, KCl as salt) has been performed by Serr. Block did symmetric CPT measurements on silica surface under the same conditions as in this work.
9.2 Forces–distance between PEI surfaces

The branched PEI cation is adsorbed from 0.1 M NaCl on negatively charged silica and leads to a charge reversal. Because of its homogeneous surface coverage, PEI is often used as a precursor layer in polyelectrolyte multilayer films. The forces between PEI surfaces were analyzed with AFM by the CPT. The mean force profiles were calculated from averaging between 100–150 forces curves recorded at 3 different locations on the surface. The force profiles were measured in water with the salt concentration varying from 0 to 1 M NaCl. Only the approach force curves between two PEI surfaces as a function of the surface separation \( D \), normalized to CP radius \( R \), are shown in Fig. 9.3 (dots, left). The measured approach force profiles show a strong repulsive interaction at low ionic strength. The force decreases exponentially with \( D \). A short-range repulsive interaction occurred at high ionic strength and the retraction force profiles show adhesion forces. These negative forces are caused by bridging of PEI molecules at the contact between the two surfaces [Pericet-Camara, 2006]. By reducing the ionic strength to 1 and 0.1 mM after 1 M, the force-distance curves show good reversibility. The addition of water again shows attraction at relatively small separation. The reason for this is not clear and needs to be explored further (Fig. 9.3(dots, left)).

![Figure 9.3:](image)

**Figure 9.3:** (Left). The force-distance profiles (dots) measured between silica CP covered with PEI and PEI surface (physisorbed from 0.1 M NaCl) at the different ionic strengths \( I \) (indicated arrows) and the corresponding linear fits according to the DLVO theory for the electrostatic forces of electric double layer (solid lines, left) using the constant potential approximation. The backward decreasing of the ionic strength (right) at 1 and 0.1 mM shows good reversibility measurement, but pure water needs further exploration.

The simple exponential decay fit (Eq. 9.1) using the constant potential approximation was applied to the approach force measurements as shown in Fig. 9.3 (lines).
Appendix

The fitting parameters, surface potential $\psi_{0,\text{PEI}}$, decay length $\lambda^{-1}$ and surface charge density $\sigma_{0,\text{PEI}}$ are summarized in Fig. 9.4 and (Tab. 9.3). The repulsive forces between PEI surfaces are well described using the Debye-Hückel approximation as expected. The experimentally determined $\lambda^{-1}$ of the PEI surfaces show good agreement with the theoretical predictions for each NaCl concentration. The electrostatic interaction confirms that PEI is flatly adsorbed on the substrate.

![Graphs showing decay length, surface potential, and surface charge density vs. ionic strength](image)

**Figure 9.4:** (Top left) The Debye length and the surface potential (top right) between two PEI surfaces fitted using the force-distance profiles and (Fig. 9.1) for silica and Eq. 9.1 of simple exponential DH which shows a dependence on the ionic strength $I$. The surface charge density $\sigma_{0,\text{PEI}}$ is calculated by applying Grahame’s equation, (Eq. 9.2), to the fitted $\psi_{0,\text{PEI}}$ (bottom).

These force-distance profiles between PEI surfaces are well described with the Debye-Hückel approximation except for surface separation smaller than 2 nm. PEI is a weakly positively charged polyelectrolyte. Grahame’s equation is used to calculate the surface charge density. A small deviation from $2.3 \text{ mC/m}^2 = \frac{e}{70 \text{ nm}^2}$ is observed. The surface charge density increases with increasing NaCl concentration. These fitting parameters for this system are compared with previous work by Berg [2014]. In this work, a slightly lower surface potential is measured. Berg used the
same approach, but the PEI was adsorbed from free salt, which may lead to higher surface potential (Tab.9.4).

<table>
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<th>$\lambda_{meas.}^{-1}$ [nm]</th>
<th>$\psi_{0,PEI}$ [mV]</th>
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**Table 9.3:** The electrostatic parameters obtained from the force-distance measurements (Fig.9.3) fit according to (Eq.9.1): comparison of the expected Debye length and measured decay length is shown in the second and third column respectively. The measured surface potential of PEI $\psi_{0,PEI}$ at different ionic strength is shown in the fourth column. The last column shows the surface charge density $\sigma_{0,PEI}$ as obtained by Grahame’s equation, (Eq.9.2), to $\psi_{0,PEI}$.

<table>
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<tr>
<th>$I_{NaCl}$ [mM]</th>
<th>$\psi_{0,PEI}$ [mV]</th>
<th>$\sigma_{0,PEI}$ [mC/m$^2$]</th>
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**Table 9.4:** Compression of surface potential $\psi_{0,PEI}$ and surface charge density $\sigma_{0,PEI}$ of PEI in this work and Berg’s work Berg [2014]. Berg did also symmetric CPT measurements of PEI surfaces adsorbed from salt-free solution.
9.3 Surface forces of PSS terminated polyelectrolyte multilayers

9.3.1 PEI / PSS / [PDADMA / PSS] terminated with PSS and PDADMA

Table 9.5: Comparison between the fitted parameters of three different surfaces covered with, PDADMA, PEI / PSS / [PDADMA / PSS], and PEI / PSS / [PDADMA / PSS] / PDADMA (physorbed from 100 mM NaCl solution) using the direct force profiles (Fig. 6.1). The surface potential $\psi_0$ and the Decay length $\lambda^{-1}$ are fitted using (Eq. 6.1). Decay length at different NaCl concentrations indicated that the three surfaces are adsorbed flatly compared to the theoretical Debye length $\kappa^{-1}$ (Eq. 3.21). The surface charge density $\sigma_0$ is calculated by Grahame’s equation, (Eq. 6.2), to the fitted $\psi_0$.

<table>
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<th>$\lambda^{-1}$ [nm]</th>
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</table>

Table 127
9.3.2 PEI / PSS / [PDADMA / PSS]$_{17}$ with PSS terminated film

Figure 9.5: Force-distance profiles (dots, obtained by averaging over 150 approach curves) acting between silica CP covered with PEI and PEI/PSS/ [PDADMA/PSS]$_{17}$ film (physisorbed from 0.1 M NaCl) with PSS as a top layer. The FCs recorded in sequence with increasing NaCl concentrations in water (arrows) from 0 M to 1 M (top left) then decreased again to 1 and 0.1 mM, then pure water again (top right). At 0.1 M small adhesion forces appeared indicating a collapse of the film top layer. The FCs are fitted to the linear DLVO theory (solid lines, (Eq. 6.3)) of the electrostatic double layer for repulsion interaction between two surfaces. The tapping mode images in the air of the dry film before (bottom left, surface roughness = 1.16 nm) and after FC measurements (surface roughness = 0.96 nm, bottom right).
Figure 9.6: The fitted parameters of PEI/PSS/ [PDADMA/PSS]_{17} film (physisorbed from 0.1 M NaCl). The decay length $\lambda^{-1}$ (top left) and surface potential, $\psi_{0,PSS}$ (top right) and are fitted by the force-distance profiles Fig. 9.5 and DLVO theory (Eq. 6.3). The fitting parameters of PEI surface in (Tab. 9.3) are used to calculate the surface potential of PSS, $\psi_{0,PSS}$. The decay length at 0 to 10 mM NaCl concentration indicated that the top layer of the multilayer film is adsorbed flatly since the decay length is within error identical to the theory (top left, solid line), and positively charged. The surface charge density, $\sigma_{0,PSS}$ (bottom) is calculated by applying Grahame’s equation, (Eq. 6.2), to the fitted, $\psi_{0,PSS}$.

9.3.3 PEI / PSS / [PDADMA / PSS]_{17} / PDADMA with PDADMA terminated film

In this part, the number of layer pairs $N = 17$ of polyelectrolyte multilayer film with PDADMA as a top layer will be introduced. As it is observed in the previous part, force-distance profiles (dots, obtained by averaging over 150 approach curves) acting between silica CP covered with PEI and PEI / PSS / [PDADMA / PSS]_{17} / PDADMA film (physisorbed from 0.1 M NaCl) with PDADMA as a top layer.
Figure 9.7: Force-distance profiles (dots, obtained by averaging over 150 approach curves) acting between silica CP covered with PEI and PEI / PSS/ [PDADMA/PSS]$_{17}$ film (physisorbed from 0.1 M NaCl) with PDADMA as a top layer. The FCs were recorded in sequence with increasing NaCl concentrations in water (arrows) from 0 M to 0.1 M (top left). The PDADMA top layer reswelled again by decreasing the ion concentration to 1 mM and pure water respectively (top right). The FCs are fitted to AdG theory for the asymmetric case (solid lines, Eq.6.6). The tapping mode images in air for the dry film before (bottom left, surface roughness = 1 nm) and after FC measurements (surface roughness = 1.5 nm, bottom right).
Appendix

Figure 9.8: Steric parameters obtained by fits to the AdG theory from the force profiles shown in Fig. 9.7 (top left). The average distance $s$ between the pseudo-tails is almost constant during salting in measurements with a small decrease at 0.1 M (left). The top layer PDADMA swells, shrinks, and reswells reversibly and a brush thickness corresponding to 15-20% of the contour length is observed at $I_{NaCl} = 1$ mM (right) which indicates that part of the PDADMA chains protruding into solution and the rest build a complex with the PSS chain inside the multilayer film.

9.4 PEI surfaces with gold

Figure 9.9: The AFM tapping mode height images ($1 \times 1 \mu m^2$) of gold nanoparticles (AuNPs) adsorbed onto PEI functionalized surfaces for (a) 15 min, (b) 45 min and (c) 197 min. PEI was physisorbed from a solution containing 2 mM PEI and 2 mM FeSO$_4$. All measurements are performed in air. Scale bars: 200 nm.
Figure 9.10: Surface coverage of AuNPs versus the square root of adsorption time. The AuNPs are adsorbed onto differently prepared PEI layers. The adsorption solution consisted of (top) 2 mM PEI, (middle) 2 mM PEI and 2 mM FeSO₄ and (bottom) 2 mM PEI, 4 mM FeSO₄ and 5 mM EDTA. The slope is fitted linearly; a horizontal line indicates saturation. The diffusion constants are calculated from the linear slope, according to Eq. 4.23.
Figure 9.11: Extinction spectra of gold nanoparticles (AuNPs) adsorbed onto PEI-functionalized surfaces physisorption from a solution containing: 4 mM FeSO$_4$ and 5 mM EDTA (olive, pH = 3), salt-free (blue, pH = 9.3), 2 mM FeSO$_4$ (orange, pH = 4.67). Extinction spectra of AuNPs adsorbed onto 2 mM PEI solution with pH = 3.19 which was adjusted using HCl (brown). AFM tapping mode image performed in air (1 × 1 μm$^2$) of AuNPs corresponding to the brown extinction spectra.

<table>
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<th>$l_1$</th>
<th>$\rho_1$</th>
<th>$l_2$</th>
<th>$\rho_2$</th>
<th>Electrons</th>
<th>PEI monomers</th>
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<tr>
<td>immersed in FeSO$_4$ solution</td>
<td>28.8</td>
<td>0.381</td>
<td>24.7</td>
<td>0.06</td>
<td>1244</td>
<td>51.8</td>
</tr>
<tr>
<td>(bottom)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 9.6: Parameters of the slab model used to fit the three X-ray reflectivity curves shown in Fig. 7.11. Electrons in both layers, PEI calculated with the assumption PEI is pure in the adsorbed film, i.e., neither water nor any ions present.

From the reflectivity curves, electron density profiles were derived. It was assumed that the PEI film consists of one slab with an electron density $l$ and a thickness $dl$. The electron density profiles of the first two films are very similar, the films have the same thickness (about 1.8 nm), and a very similar maximum electron density (0.29 e$^-$/Å$^3$ and 0.28 e$^-$/Å$^3$). These values are below the electron density of water, they can be explained by a loosely packed PEI film. However the third film is very
different. Its electron density was modelled by a two slab model. The film shows a large maximum electron density (0.381 e⁻/Å³) which is larger than the electron density of water (0.334 e⁻/Å³). Therefore, it is suggested that in this film Fe²⁺ is incorporated. Furthermore, the film thickness increased substantially to about 5 nm (cf. Tab. 9.6).
Publications

Articles
Stefanie Perfahl, Marta M. Natile, Heba S. Mohamad, Christiane A. Helm, Carola Schulzke, Giovanni Natile, and Patrick J. Bednarski
Photoactivation of Diiodido–Pt(IV) Complexes Coupled to Upconverting Nanoparticles, Molecular pharmaceutics, 2016, 13, 2346-2362
Henrik Rebla, Birgit Fink, Jürgen Schmidt, Heba S. Mohamad, Roland Ihrke, Christiane A. Helm Barbara Nebea
Accelerated Cell-Surface Interlocking on Plasma Polymer-Modified Porous Ceramics, Materials Science and Engineering: C, 2016, 69, 1116-1124

Talks
Heba Soker Mohamad, Sven Neuber, and Christiane A. Helm
How to tune the surface forces of PDADMA terminated polyelectrolyte multilayers, DPG-Frühjahrstagung (DPG Spring Meeting), Berlin, 11 - 16 March 2018

Heba S. Mohamad, Sven Neuber, Annkatrin Sill, and Christiane A. Helm
Surface forces of polyelectrolyte multilayers in different growth regimes, DPG Spring Meeting, Dresden, 19 - 24 of March 2017

Heba S. Mohamad, Heiko Ahrens, and Christiane A. Helm
Long-ranged steric forces between physisorbed polyethylenimine-iron complexes, 80th Annual Conference of the DPG and DPG Spring Meeting, Regensburg, 6 - 11 March 2016

Poster
Heba Soker Mohamad, Sven Neuber, Annkatrin Sill, and Christiane A. Helm
A wide range of surface forces of PSS terminated polyelectrolyte multilayers, DPG-Frühjahrstagung (DPG Spring Meeting), Berlin, 11 - 16 March 2018
Neha Jha, Christian Denker, Anand Paryar, Pavan K. Vardhanapu, Heba S. Mohamad, Ulrike Martens, Christiane A. Helm, Swadhin Mandal, and Markus Münzenberg

High TMR at Room Temperature in Magnetic Tunnel Junctions with Phenalenyl-molecule Tunnel Barriers, DPG-Frühjahrstagung (DPG Spring Meeting), Berlin, 11 - 16 March 2018,

Christian Denker, Pavan K. Vardhanapu, Bikash Das Mohapatra, Ulrike Martens, Heba S. Mohamad, Mykola Medvidov, Christiane A. Helm, Swadhin Mandal, and Markus Münzenberg

PLY-Cu for organic MTJs, PG Spring Meeting, Dresden, 19 - 24 of March 2017

Heba S. Mohamad, Peter Nestler, Harm Wulff, Stefanie Perfahl, Patrick Bednarski, and Christiane A. Helm

AFM and physicochemical characterization of Upconversion Nanoparticles, DPG-Frühjahrstagung (DPG Spring Meeting), Regensburg, 10 - 15 March 2013

Stefanie Perfahl, Patrick Bednarski, Marta M. Natile, Heba S. Mohamad, Christiane A. Helm

Erklärung


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